ARIZONA DEPARTMENT OF ENVIRONMENTAL QUALITY

Proposal of a Total Maximum Daily Load For:
Three-R (3R) Canyon, Sonoita Creek Basin,
Santa Cruz River Watershed,
Coronado National Forest,
near Patagonia, Santa Cruz County, Arizona

HUC: 15050301-558A
Parameters: **Beryllium, Cadmium, Copper, Zinc and Acidity**

Prepared: February 10, 2003

APPROVALS

Prepared & Submitted by:____________________________ Date:_________
Robert Scalamera, Hydrologist, TMDL Unit

Approved by:_____________________________________ Date:_________
Nancy LaMascus, Supervisor, TMDL Unit

Approved by:_____________________________________ Date:_________
Linda Taunt, Manager, HSA Section

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Note: ADEQ has rewritten this report based on comments submitted in response to the previous (12/06/01) report and to reflect changes in Arizona's Surface Water Quality Standards resulting from the 2002 triennial review.

Project Manager: Robert J. Scalamera, Hydrologist
Arizona Department of Environmental Quality
Water Quality Division
Hydrologic Support & Assessment Section, TMDL Unit
E-mail: scalamera.robert@ev.state.az.us
Telephone: (602) 771-4515

Mail Address: Arizona Department of Environmental Quality
Water Quality Division
Hydrologic Support & Assessment Section, TMDL Unit
Robert J. Scalamera / Mailstop 5415A-1
1110 W. Washington St.
Phoenix, Arizona 85007

ACRONYMS

ADEQ Arizona Department of Environmental Quality

HEC-HMS Hydrologic Modeling System produced by the U.S. Army Corps of Engineers, Hydrologic Engineering Center, Sacramento, California

CERCLA Comprehensive Environmental Response, Compensation, and Liability Act, commonly known as Superfund

CWA Clean Water Act

HUC Hydrologic Unit Code

LA Load Allocation (Non-Point Sources)

MOS Margin of Safety

NPDES National Pollutant Discharge Elimination Systems (CWA source permits program)

TMDL Total Maximum Daily Load

USEPA United States Environmental Protection Agency (also EPA)

USGS United States Geological Survey

USFS United States Forest Service

WLA Waste Load Allocation (Point Sources)

WQS Water Quality Standards (AZ)

cfs cubic feet per second (commonly used discharge measurement unit)

ft feet

mg/L milligrams per liter (pollutant concentration measurement unit)

Fg/L micrograms per liter (pollutant concentration measurement unit)

kg/day kilograms per day (pollutant load measurement unit)

DEFINITIONS OF TERMS USED IN THIS REPORT

Bankfull (discharge)	The flow in the stream at the point of incipient flooding; i.e., the largest non-flood discharge.
Baseflow (discharge)	The perennial portion of the stream discharge; the flow not directly dependent on precipitation events. In the case of an ephemeral stream, baseflow equals zero.
Ephemeral	A stream that has a channel that is at all times above the water table and that flows only in direct response to precipitation
Intermittent	A stream or reach of a stream that flows continuously only at certain times of the year, as when it receives water from a spring or from another surface source, such as melting snow. (AAC R18-11-101(30))
Mining Residue	Residue that is a result of mine related activities and takes the form of waste material piles and spills.
Perennial	A surface water which flows continuously throughout the year. (A.A.C. R18-11-101(38))
Point source	Any discernible, confined, and discrete conveyance, including but not limited to any pipe, ditch, channel, tunnel, conduit, well, discrete fixture, container, rolling stock, concentrated animal feeding operation, landfill leachate collection system, vessel, or other floating craft from which pollutants are or may be discharged. (40 CFR 122.2)
Significant Mining	Mine related activities which result in an observable impact, such as adit drainage or a large volume of exposed mining residue.

NOTE: ADEQ uses USGS maps as the source of names for streams, mines, and other features. Where local usage varies, such differences are noted.

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1.0 PREFACE

1.1 The Clean Water Act (CWA) §303[d] and Its Significance

The CWA §303[d][1][A] requires that "Each State shall identify those waters within its boundaries for which the effluent limitations...are not stringent enough to implement any water quality standard applicable to such waters." This act also requires states to establish Total Maximum Daily Loads (TMDLs) for such waters.

The CWA §303[d] requires states to submit to the United States Environmental Protection Agency (USEPA) a list of the surface waterbodies for which the designated use (e.g. irrigation, partial body contact, etc.) of that waterbody is impaired or "water quality limited". Surface water quality data are compared with water quality standards and other criteria to determine whether the waterbody is meeting its designated uses. ADEQ publishes a report on the status of surface water and groundwater quality in Arizona every two years (in accordance with the CWA §305(b)) and from this report derives the "Impaired Waters" or "303[d] List".

The TMDL process provides a flexible assessment and planning framework for identifying load reductions or other actions needed to attain surface water quality standards; i.e. water quality goals to protect aquatic life, drinking water, and other water uses. The CWA established the TMDL process to guide application of state surface water quality standards to individual waterbodies and their watersheds.

1.2 TMDL Defined

The requirements of a TMDL analysis are described in 40 CFR §130.2 & §130.7, based upon CWA §303[d]. A TMDL is described as "the sum of the individual wasteload allocations for point sources and load allocations for non-point sources and natural background" and a margin of safety such that the capacity of the waterbody to assimilate pollutant loadings is not exceeded. Represented as a mathematical equation:

TMDL = WLA + LA + MOS,

where WLA is the wasteload allocation consisting of loads from point sources, LA is the load allocation consisting of non- point source loads, and MOS is a Margin of Safety which serves to address uncertainties in the analysis and the natural system.

1.3 The TMDL Process

A TMDL analysis is a tool for implementing state surface water quality standards and is based on the relationship between pollution sources and in-stream water quality conditions. The TMDL process is a method used in balancing the pollution concerns for a waterbody and allocating the acceptable pollutant loads among the different point and non-point sources allowing the selection and implementation of suitable control measures to attain water quality standards.

In implementing TMDLs, certain criteria must be taken into account. These criteria include loading capacity, load allocation, wasteload allocation, natural background, and the margin of safety. The loading capacity is the greatest amount of loading that a waterbody can receive without violating water quality standards. Load allocation is the portion of a receiving water's loading capacity that is attributed either to one of its existing non-point sources of pollution or to natural background sources. The portion of the receiving waters' loading capacity that is attributed to existing point sources of pollution is known as the wasteload allocation. Finally, the margin of safety is the factor that accounts for any uncertainty in the relationship between the pollutant loads and the quality of the receiving waterbody (40 CFR §130.2[f-g]). Total pollutant loads are determined by combining the point, non-point and background sources of pollution.

ADEQ has adopted a stakeholder process for many of its programs, including TMDLs. ADEQ works closely with affected stakeholders in developing the TMDL by holding meetings to solicit input on a variety of topics including background information; potential modeling scenarios; identifying possible pollutant sources for allocation; and discussing potential implementation strategies. Once TMDLs are developed for all the water quality problems, they are submitted to the EPA for review and approval.

The TMDL process is not complete once wasteload allocations and load allocations have been determined. Assessment of the TMDL effectiveness must be made. Ideally, this would begin within two years after implementation and continue for the period necessary to measure effectiveness.

1.4 Project History

ADEQ performed this investigation of Three-R (3R) Canyon in response to the stream being listed for violations of water quality standards on the 1996 and 1998 303[d] Lists. Because 3R Canyon is one of three stream segments in the Sonoita Basin that was listed on the State’s 303[d] List of impaired waters, ADEQ decided to perform investigations of these segments simultaneously. The other waterbodies in this study are Alum Gulch and Upper Harshaw Creek. This project was started in 1997 and site monitoring was performed between 1997 and 2000 by ADEQ staff.

In 2000, ADEQ hired Hydro Geo Chem (HGC) of Tucson, AZ to review available data, select an appropriate model, and conduct flow and load modeling for the three listed segments within the Sonoita Basin. HGC used ADEQ field measurements to support modeling. The first draft of this TMDL investigation was based solely on ADEQ field measurements and modeling performed by HGC. It was released for public review in December, 2001 and it received considerable public comment.

In the spring of 2002, the USGS completed a six year long study in the Sonoita Basin. USGS staff has made available to ADEQ staff all monitoring data and findings which would be considered pertinent to the three TMDL investigations. All references to their data and findings included herein were received through personal communication with USGS staff. Currently, results from their investigation are being synthesized into a draft report.

After the public review period, when the USGS data and findings became available, ADEQ tasked HGC with reviewing this information and updating the model as necessary. HGC determined that the USGS data supported and enhanced ADEQ's understanding of pollutant sources and critical conditions; however, the USGS data did not offer new flow related events which could be used in the model. ADEQ revised the report based on this additional analysis. Additionally, USEPA approved ADEQ’s proposed 2002 triennial review changes to surface water quality standards. The TMDLs were recalculated using the new standards and applicable revised designated uses. This draft of the report incorporates the additional data and changes to Arizona’s water quality standards.

2.0 PHYSICAL SETTING

2.1 Overview

The 3R Canyon Basin is in Santa Cruz County, Arizona. The closest town is Patagonia, Arizona. The approximate center of the basin is, latitude: 31E 28'N, longitude: 110E 47' W. Basin elevation ranges from 6,400 ft. to 4,000 ft. The subject reach (the 303[d]-listed reach) is referred to as "upper 3R Canyon" for the purposes of this project. The primary tributary to the listed portion of 3R Canyon is Cox Gulch and an unnamed canyon tributary to Cox Gulch. There are no active mines in the subject basin. Figures 1, 2, and 3 provide views of the project location, overall area, and the subject basin.

As noted above, for purposes of this study, there are two distinct sections to upper 3R Canyon:

- the 3R Canyon section which can be further divided into:
  - headwaters above the 3R Mine (natural background);
  - the 3R Mine complex, and;
  - the intermittent reach beginning at a spring approximately 800 meters downstream from the 3R Mine and continues to the bottom of the listed reach where it meets Cox Gulch.

- the Cox Gulch section which can be further divided into:
  - upper Cox Gulch, containing the Ventura Mine;
  - the un-named tributary containing the European Mine (unofficially named the European Mine tributary for purposes of this study);
  - the approximately 250 meter-long intermittent step-pool reach fed by a spring, and;
  - the lowest portion of Cox Gulch which is ephemeral.

2.2 Climatology

The climate of the 3R Canyon basin varies from high desert in the Sonoita Valley to the steppe-like climate of the higher elevation grasslands and scrub forest. Below-freezing temperatures are to be expected during the winter months, and precipitation, both rain and snow, occurs most winters. Most summers bring "monsoon" thunderstorms. Snow may remain on the higher elevations for periods ranging from hours to weeks. The closest weather stations to the subject basin, at Canelo Pass, Nogales, and San Rafael Ranch, have different climatic settings (e.g., elevation, position relative to mountains) and do not accurately reflect the conditions found in the upper 3R Canyon basin.

2.3 Hydrology

The approximately 5 mile segment (upper 3R Canyon) is primarily ephemeral with one intermittent stretch beginning at a spring located approximately 800 meters downstream from the 3R Mine. During baseflow conditions, when runoff was not present, flow from the spring was observed to flow intermittently over a one mile segment to the end of the subject reach at the mouth of Cox Gulch. The approximately 2 mile long Cox Gulch and its tributaries is also ephemeral with the exception of an approximately 250 meter long, spring-fed, step-pool segment formed just downstream of the confluence of the European Mine tributary with Cox Gulch. Based upon field observations, groundwater (from the springs) is the sole source of flow during baseflow conditions.

Measured and modeled discharges on the subject reach varied from 0.001 to 42.5 cfs. Upper 3R Canyon drains approximately 1,770 acres and no flow gaging stations exist on the subject waterbody. Field observations confirm that all of the tributaries to upper 3R Canyon are ephemeral, except at the noted spring sources. During the 2002 ADEQ triennial review of standards, a flow-related designated use change, from perennial to ephemeral, was adopted for upper 3R Canyon from its headwaters to approximately 800 meters downstream of the 3R Mine (which begins a one-mile spring-supplied intermittent reach).

2.4 Geology

The Three R Canyon Basin lies within the Basin and range physiographic province. This province, typified by north-northwest trending normal faults, has broad, gentle sloping valleys, such as the upper Sonoita Creek valley, separated by sharply rising mountain ranges. The USGS map and sections of the Nogales and Lochiel quadrangles show the notable structures affecting this basin include two northwest-trending faults. An unnamed concealed northwest trending fault appears on the western edge of this basin. The Harshaw Creek Fault, a north-northwest trending left-lateral strike-slip fault lies just to the east of the basin in Flux Canyon. The Harshaw Creek Fault, thought to be associated with the Laramide Orogeny, shows more than 4 miles of displacement at its southernmost end.

Sizeable irregularly shaped pods of the Mount Wrightson Formation, a Triassic rhyolitic to latitic lava and tuff are stretched across the center of this basin in a north-northwest trend. Along the eastern edge of the basin, a long narrow strip of Jurassic/Triassic monzonite porphyry, which intruded the Mount Wrightson Formation, parallels the Harshaw Creek Fault. The rest of this basin is comprised by the Granite of Comoro Canyon. In the basin's central and middle section, the Granite of Comoro Canyon is an equigranular quartz-rich granite which is "pervasively sericitized and pyritized" as seen at three R and in Cox Gulch. In the southern and southwestern portion of the basin, the Granite of Comoro Canyon is an equigranular alkali syenite.

The three prominent mines in this watershed, the Three R, European and Ventura Mines, are located along a ridge which sits at the western edge of a porphyry system. The porphyry is aerially extensive but the polymetallic ore is local to veins which are mined at depth. Ore deposition occurred during the Laramide Orogeny (Cretaceous to early Tertiary). Associated skarns also host minerals of economic significance. An oxide rind, extending 30-45 feet subsurface, has developed in the vein deposits (personal comm, Floyd Gray, USGS, 07/25/2002, 01/24/03).

2.5 Vegetation/Wildlife

Upper 3R Canyon flows through a narrow steep-walled valley with little vegetation on the floodplain. The hillsides are covers with oak, mesquite, yucca and ocotillo. Where the valley widens and has a flat layer of alluvium (terrace), it is vegetated with the cottonwoods, sycamores, willows, and other plants typical of arid area riparian zones.

A review of the U.S. Fish and Wildlife Service web site did not reveal the presence of threatened or endangered species in the subject basin.

2.6 Land Use/Land Ownership

The upper 3R Canyon Basin is almost wholly contained within the Coronado National Forest and is available for recreational usage and limited cattle grazing. The Upper 3R Canyon Basin contains one privately owned mine, the 3R Mine complex, which is owned (but never operated) by James “ Buck” Clark.

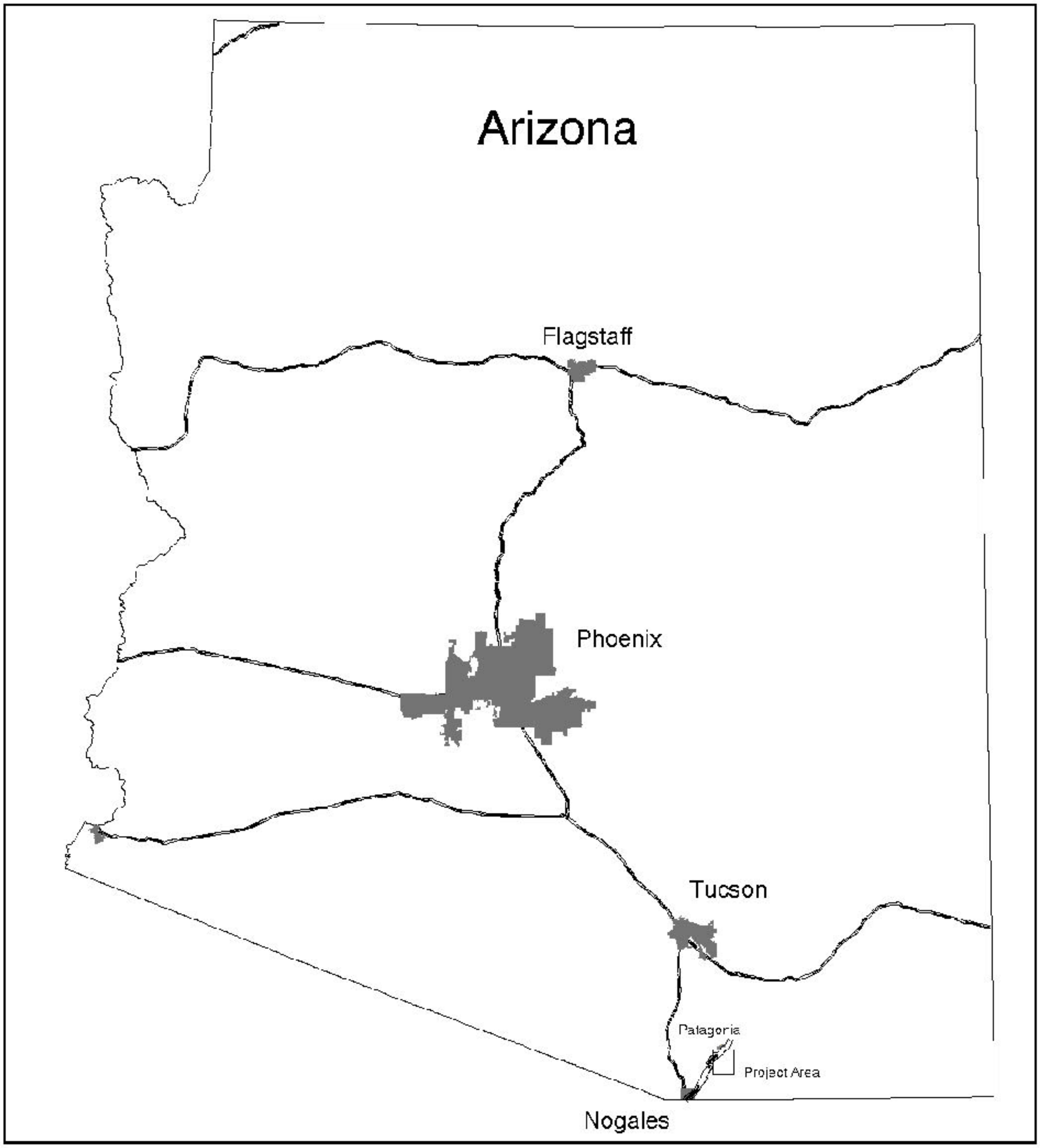
The upper 3R Canyon Basin contains areas of mineralization (primarily zinc, lead and copper) that have been mined since prior to the arrival of the first Spanish explorers, approximately 500 years ago (Arizona Department of Mines and Minerals; Sheila Dean, USFS). Large-scale mining, consisting of mainly sub-surface workings, began in the mid-1800s and continued for approximately 100 years. The region is covered with abandoned mine workings; small, shallow exploration pits and mining residue.

There is some privately owned land occupied by the Circle Z ranch in lower 3R Canyon Basin downstream from the study area.

2.7 Problem Statement

This segment was listed for impairments due to beryllium, copper, zinc, and acidity (low pH). As a result of monitoring for this study, it was found that the streams also were impaired for cadmium which was added to the 2002 303(d) list, published by ADEQ in October, 2002. The overall purpose of this project was to provide an assessment of the sources of these pollutants and to calculate TMDLs for listed pollutants on the affected reaches. Lower 3R Canyon, starting at the downstream end of the study reach (the confluence of Cox Gulch and upper 3R Canyon) and continuing approximately 3 miles to its mouth on Sonoita Creek, is not included on the 303[d] List and, therefore, not addressed in this TMDL.

Flow in upper 3R Canyon carries measurable quantities of total beryllium, dissolved copper, dissolved zinc, dissolved cadmium, and has excessively low pH. The pollutants of concern result from the chemical weathering of sulfide-mineralized rock which produces sulfuric acid. Sulfuric acid acts to disassociate metals from the mineral matrix and make them available for transport, in the dissolved form, in the water column. Sulfide minerals are naturally occurring in the mining district. They can also be found in stockpiled mine materials.



Not to Scale

N

Figure 1 - Project Location
Sonoita Creek Basin TMDL Projects

Bob Scaamera
ADEQ/WQD/HSAS/TMDL Unit
10/22/01

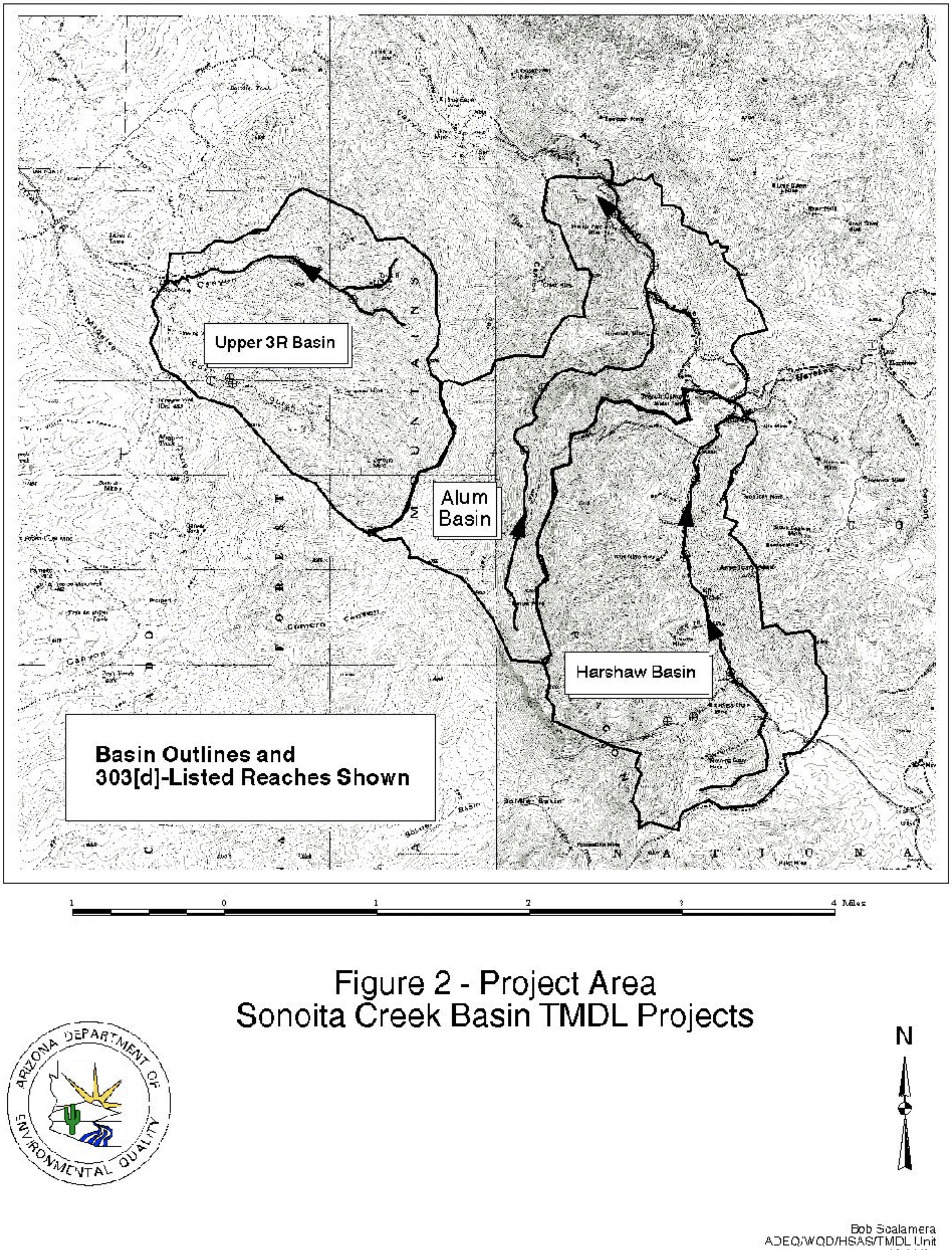


Figure 2 - Project Area
Sonoita Creek Basin TMDL Projects

3.0 NUMERIC TARGETS

3.1 Surface Water Quality Standards

The State of Arizona has adopted numeric water quality standards (Table 1) which protect the designated uses of each surface water. During the 2002 triennial review of surface water quality standards, ADEQ modified designated uses for several segments within the study area. The State also repealed the chronic water quality standards on ephemeral waters; therefore, only the acute standards apply to ephemeral waters. The revised standards were approved by the USEPA on October 22, 2002.

For upper 3R Canyon, from its headwaters to approximately 800 meters downstream of the 3R Mine; most of Cox Gulch and its tributaries, the following designated uses apply:

- Aquatic and Wildlife ephemeral (A&We),
- Partial Body Contact (PBC), and
- Agricultural Livestock Watering (AgL).

For upper 3R Canyon from approximately 800 meters downstream of the 3R Mine to its confluence with Cox Gulch; and the step-pool segment in Cox Gulch, the following designated uses apply:

- Aquatic and Wildlife warm water (A&Ww),
- Full Body Contact (FBC),
- Fish Consumption (FC), and
- Agricultural Livestock Watering (AgL).

The numeric target for each of the listed pollutants has been set so that the most stringent water quality standard for the supported designated uses can be supported. The copper, cadmium, and zinc standards for the listed Aquatic and Wildlife uses vary with hardness (range of 25 to 400 mg/L as $CaCO_3$) (A.A.C. Title 18, Chapter 11, Article 1, App. A).

Table 1 Surface Water Quality Standards (basis for numeric targets)

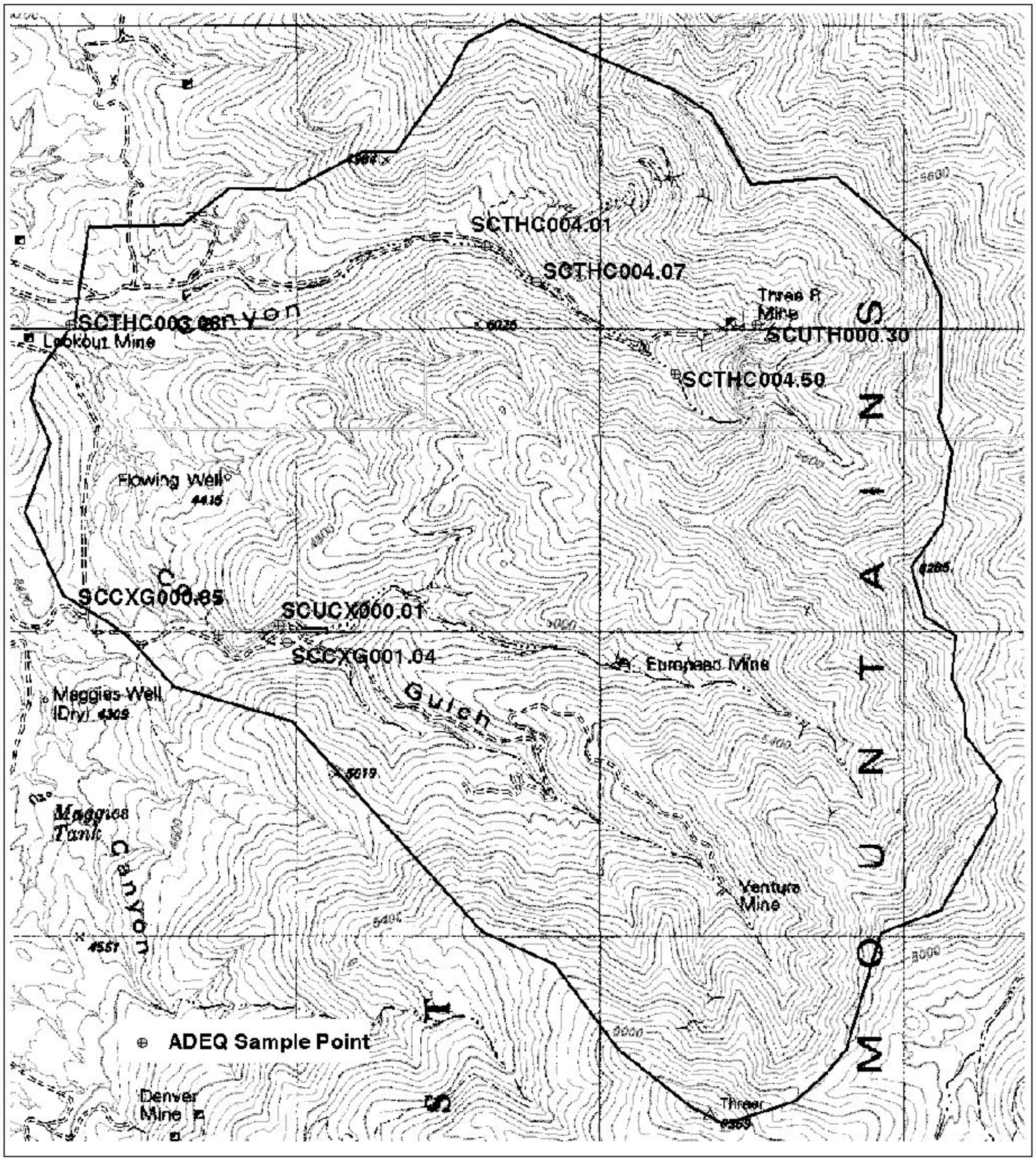
	pH	Beryllium (Fg/L)		Cadmium (Fg/L)		Copper (Fg/L)		Zinc (Fg/L)	
Designated Use		Total	Diss	Total	Diss	Total	Diss	Total	Diss
A&Ww, chronic	6.5 - 9.0	--	5.3	--	0.80 -6.2	--	2.7 -29	--	36 - 379
A&We, acute	6.5 - 9.0	--	--	--	14 - 290	–	6.3 - 86	–	344 - 3,599
FBC/PBC	6.5 - 9.0	2,800	--	700	--	1,300	--	420,000	--
FC	6.5 - 9.0	1,130	--	84	--	--	--	69,000	--
AgL	6.5 - 9.0	--	--	50	--	500	--	25,000	–

The minimum applicable pH standard, as shown above, is 6.5. Since this is a unitless number, it was converted to H+ ion concentration in Fg/L for the load calculations. The formula is $10^{(-pH)}$ which results in a hydrogen concentration in moles and, since the atomic weight of hydrogen is one, this equates very closely to mg/L. Multiplying by 1,000 gives hydrogen ion concentration in Fg/L. Using this formula, the H+ concentration of 0.00032 Fg/L is equivalent to the standard of 6.5. The larger the H+ concentration, the lower the pH.

Tables 2A-2E include a summary of measured concentrations in comparison to applicable standards. Figure 3 displays the relative locations of ADEQ and USGS sample sites.

3.2 In-stream Indicators

Reliable in-stream indicators that are solely related to water quality have not been observed in the subject watershed. The "normal" indicators (i.e., insects, fish, and vegetation) are also adversely affected by the huge variations in water quantity (dry to flood). The presence of evaporative salts (precipitates) on the dry portions of the streambed may be considered in-stream indicators, but much more data needs to be collected to determine and quantify the relationship to in-stream water quality. Attributing a cause to an in-stream indicator is therefore tenuous at best. Hillslope conditions hold some promise as indicators, but, again, much more data needs to be collected to determine and quantify the relationship to in-stream water quality. Therefore, for this phase of the TMDL, ADEQ has chosen to rely solely on in-stream concentrations of the pollutants of concern.



From USGS 7.5', "Cumero Canyon, AZ"

1 0 1 Miles

Figure 3 - 3R Canyon TMDL Project Sample Points

Bob Scalamera
ADEQ/WQD/HSAS/TMDL Unit
02/05/03

POLLUTANT MONITORING DATA

Table 2A pH Data (standards exceedences in bold)

Site	Date	Discharge (cfs)	pH WQS	pH Data
SCUTH000.30 (nat back)	07/21/99	0.17	6.5 - 9.0	**3.8**
SCTHC004.50 (nat back)	07/21/99	0.08	6.5 - 9.0	**3.7**
SCTHC004.07	07/21/99	0.05	6.5 - 9.0	**3.5**
SCTHC004.01[1]	12/05/97	0.001 (est)	6.5 - 9.0	**2.9**
SCTHC004.01[1]	02/04/98	0.04	6.5 - 9.0	**2.9**
SCTHC004.01[1]	04/01/98	0.02	6.5 - 9.0	**3.0**
SCTHC004.01[1]	06/01/98	0.001 (est)	6.5 - 9.0	**3.1**
SCTHC004.01[1]	07/21/99	0.02	6.5 - 9.0	not meas [2]
SCTHC004.01[1]	01/11/00	0.001 (est)	6.5 - 9.0	**2.9**
SCCXG001.04	07/21/99	0.01	6.5 - 9.0	not meas [2]
SCUCX000.01	07/21/99	0.23	6.5 - 9.0	not meas [2]
SCCXG000.85[1]	07/21/99	0.06	6.5 - 9.0	not meas [2]
SCCXG000.85[1]	01/10/00	0.001 (est)	6.5 - 9.0	**3.3**
SCTHC003.03[1]	02/04/98	0.93	6.5 - 9.0	**3.9**
SCTHC003.03[1]	04/01/98	0.11	6.5 - 9.0	**3.4**

Notes:

1 Intermittent reaches: A&Ww, FBC, FC and AgL designated uses apply. All other segments and tributaries are ephemeral and carry A&We, PBC and AgL uses only.

2 Not measured

Table 2B Beryllium (standards exceedences in bold)

Site	Date	Discharge (cfs)	A&Ww WQS (Fg/L)	Data Be diss (Fg/L)	FBC/PBC WQS (Fg/L)	FC WQS (Fg/L)	Data Be total (Fg/L)
SCUTH000.30 (nat back)	07/21/99	0.17	NNS[6]	ND [2,3]	2,800	--	0.7
SCTHC004.50 (nat back)	07/21/99	0.08	NNS[6]	ND [2,3]	2,800	--	0.5
SCTHC004.07	07/21/99	0.05	NNS[6]	ND [2,3]	2,800	--	ND [2,3]
SCTHC004.01[1]	12/05/97	0.001 (est)	5.3	not meas[5]	2,800	1,130	not meas [5]
SCTHC004.01[1]	02/04/98	0.04	5.3	not meas[5]	2,800	1,130	not meas[5]
SCTHC004.01[1]	04/01/98	0.02	5.3	ND [2,4]	2,800	1,130	ND [2,4]
SCTHC004.01[1]	06/01/98	0.001 (est)	5.3	ND [2,4]	2,800	1,130	ND [2,4]
SCTHC004.01[1]	07/21/99	0.02	5.3	2.1	2,800	1,130	2.4
SCTHC004.01[1]	01/11/00	0.001 (est)	5.3	4.6	2,800	1,130	5.1
SCCXG001.04	07/21/99	0.01	NNS[6]	not meas[5]	2,800	--	not meas [5]
SCCXG000.01	07/21/99	0.23	NNS[6]	9	2,800	--	8
SCCXG000.85[1]	07/21/99	0.06	5.3	**6.6**	2,800	1,130	7.4
SCCXG000.85[1]	01/10/00	0.001 (est)	5.3	**6.6**	2,800	1,130	7.2
SCTHC003.03[1]	02/14/98	0.93	5.3	**5.8**	2,800	1,130	8
SCTHC003.03[1]	04/01/98	0.11	5.3	**9.4**	2,800	1,130	12

Notes:

1 Intermittent reaches: A&Ww, FBC, FC and AgL designated uses apply. All other segments and tributaries are ephemeral and carry A&We, PBC and AgL uses only.

2 Not Detected

3 Method Reporting Limit = 0.5 Fg/L

4 Method Reporting Limit = 2.0 Fg/L

5 Not measured

6 No Numeric Standard

Table 2C Cadmium (standards exceedences in bold)

Site	Date	Discharge (cfs)	Hard [2] (calc/adj)	A&Ww WQS (Fg/L)	A&We WQS (Fg/L)	Data Cd diss (Fg/L)	FC WQS (Fg/L)	AgL WQS (Fg/L)	Data Cd total (Fg/L)
SCTHC000.03 (nat back)	07/21/99	0.17	29	--	17	ND [3,4]	--	50	ND [3,4]
SCTHC004.50 (nat back)	07/21/99	0.08	26	--	15	ND [3,4]	--	50	ND [3,4]
SCTHC004.07	07/21/99	0.05	26	--	15	1.6	--	50	1.7
SCTHC004.01[1]	12/05/97	0.001 (est)	72	1.8	--	**143**	84	50	**112**
SCTHC004.01[1]	02/04/98	0.04	43	1.2	--	**57**	84	50	**54**
SCTHC004.01[1]	04/01/98	0.02	46	1.3	--	**40**	84	50	40
SCTHC004.01[1]	06/01/98	0.001 (est)	52	1.4	--	**59**	84	50	**52**
SCTHC004.01[1]	07/21/99	0.02	43	1.2	--	**35**	84	50	42
SCTHC004.01[1]	01/11/00	0.001 (est)	63	1.6	--	**47**	84	50	49
SCCXG001.04	07/21/99	0.01	402/400	--	290	25	--	50	35
SCCXG000.01	07/21/99	0.23	261	--	182	14	--	50	12
SCCXG000.85[1]	07/21/99	0.06	292	4.92	--	**15**	84	50	35
SCCXG000.85[1]	01/10/00	0.001 (est)	927/400	6.22	--	**60**	84	50	**72**
SCCXG003.03[1]	02/04/98	0.93	206	3.82	--	7	84	50	14
SCTHC003.03[1]	04/01/98	0.11	412/400	6.22	--	**31**	84	50	33

Notes:

1 Intermittent reaches: A&Ww, FBC, FC and AgL designated uses apply. All other segments and tributaries are ephemeral and carry A&We, PBC and AgL uses only.

2 Hardness values less than 25 mg/L were adjusted to 25 mg/L; values greater than 400 mg/L were adjusted to 400 mg/L. (A.A.C. Title 18, Chapter 11, Article 1, Appendix A)

3 Not Detected

4 Method Reporting Limit = 1.0 Fg/L

Table 2D Copper (standards exceedences in bold)

Site	Date	Discharge (cfs)	Hard [2] (calc/adj)	A&Ww WQS (Fg/L)	A&We WQS (Fg/L)	Data Cu diss (Fg/L)	FBC/ PBC WQS (Fg/L)	AgL WQS (Fg/L)	Data Cu total (Fg/L)
SCTHC000.03 (nat back)	07/21/99	0.17	29	--	7.2	**1,400**	1,300	500	**1,400**
SCTHC004.50 (nat back)	07/21/99	0.08	26	--	6.5	**380**	1,300	500	370
SCTHC004.07	07/21/99	0.05	26	--	6.5	**7,200**	1,300	500	**7,700**
SCTHC004.01[1]	12/05/97	0.001 (est)	72	6.8	--	**80,900**	1,300	500	**73,700**
SCTHC004.01[1]	02/04/98	0.04	43	4.4	--	**47,200**	1,300	500	**45,200**
SCTHC004.01[1]	04/01/98	0.02	46	4.6	--	**68,500**	1,300	500	**66,100**
SCTHC004.01[1]	06/01/98	0.001 (est)	52	5.1	--	**71,900**	1,300	500	**66,000**
SCTHC004.01[1]	07/21/99	0.02	43	4.4	--	**44,000**	1,300	500	**47,000**
SCTHC004.01[1]	01/11/00	0.001 (est)	63	6.0	--	**49,000**	1,300	500	**50,000**
SCCXG001.04	07/21/99	0.01	402/400	--	86	**8,000**	1,300	500	**8,700**
SCCXG000.01	07/21/99	0.23	261	--	57	**7,600**	1,300	500	**7,600**
SCCXG000.85[1]	07/21/99	0.06	292	22	--	**8,200**	1,300	500	**8,600**
SCCXG000.85[1]	01/10/00	0.001 (est)	927/400	29	--	**18,000**	1,300	500	**18,000**
SCTHC003.03[1]	02/04/98	0.93	206	16.6	--	**12,500**	1,300	500	**14,800**
SCTHC003.03[1]	04/01/98	0.11	412/400	29	--	**36,200**	1,300	500	**34,500**

Notes:

1 Intermittent reaches: A&Ww, FBC, FC and AgL designated uses apply. All other segments and tributaries are ephemeral and carry A&We, PBC and AgL uses only.

2 Hardness values less than 25 mg/L were adjusted to 25 mg/L; values greater than 400 mg/L were adjusted to 400 mg/L. (A.A.C. Title 18, Chapter 11, Article 1, Appendix A)

Table 2E Zinc (standards exceedences in bold)

Site	Date	Discharge (cfs)	Hard [2] (calc/adj)	A&Ww WQS (Fg/L)	A&We WQS (Fg/L)	Data Zn diss (Fg/L)	FC WQS (Fg/L)	AgL WQS (Fg/L)	Data Zn total (Fg/L)
SCUTH000.30 (nat back)	07/21/99	0.17	29	--	390	ND [3,4]	--	25,000	ND [3,4]
SCTHC004.50 (nat back)	07/21/99	0.08	26	--	355	51	--	25,000	ND [3,4]
SCTHC004.07	07/21/99	0.05	26	--	355	110	--	25,000	94
SCTHC004.01[1]	12/05/97	0.001 (est)	72	89	--	**2790**	69,000	25,000	2,930
SCTHC004.01[1]	02/04/98	0.04	43	57	--	**1350**	69,000	25,000	1,350
SCTHC004.01[1]	04/01/98	0.02	46	61	--	**1240**	69,000	25,000	1,240
SCTHC004.01[1]	06/01/98	0.001 (est)	52	67	--	**1750**	69,000	25,000	1,520
SCTHC004.01[1]	07/21/99	0.02	43	57	--	**850**	69,000	25,000	900
SCTHC004.01[1]	01/11/00	0.001 (est)	63	79	--	**1400**	69,000	25,000	1,400
SCCXG001.04	07/21/99	0.01	402/400	--	3,599	**5,900**	--	25,000	6,000
SCCXG000.01	07/21/99	0.23	261	--	2,507	**2,900**	--	25,000	2,400
SCCXG000.85[1]	07/21/99	0.06	292	291	--	**3,200**	69,000	25,000	3,200
SCCXG000.85[1]	01/10/00	0.001 (est)	927/400	379	--	**11,000**	69,000	25,000	12,000
SCTHC003.03[1]	02/04/98	0.93	206	216	--	**920**	69,000	25,000	2,580
SCTHC003.03[1]	04/01/98	0.11	412/400	379	--	**5,010**	69,000	25,000	4,940

Notes:

1 Intermittent reaches: A&Ww, FBC, FC and AgL designated uses apply. All other segments and tributaries are ephemeral and carry A&We, PBC and AgL uses only.

2 Hardness values less than 25 mg/L were adjusted to 25 mg/L; values greater than 400 mg/L were adjusted to 400 mg/L. (A.A.C. Title 18, Chapter 11, Article 1, Appendix A)

3 Not Detected

4 Method Detection Limit = 50 Fg/L

4.0 SOURCE ANALYSIS

The primary project objective of this investigation was to collect data sufficient to isolate, both geographically and temporally, and quantify, relative to each other, the primary pollutant load sources in the project area. All significant sources have been identified and linkages between these significant sources and loads are discussed in the Linkage Analysis Section 5.0.

The data used to determine impairment which resulted in the 303[d]-listing was collected during the 1980s and 1990s in support of the goals of other ADEQ programs and is insufficient to isolate sources or calculate loads. As part of this project, ADEQ collected data specific to the goals of source quantification and TMDL calculation. Lack of precipitation during the study period made a comprehensive analysis of all sources impossible.

There are no known NPDES-permitted point sources in the subject basin; however, a complete review of all sources may result in the classification of some as “point sources” which would require NPDES discharge permits.

4.1 Current Conditions

Four verification sampling events were completed between December 1997 and June 1998 on upper 3R Canyon at a sample point SCTHC004.01 (the upstream end of the intermittent reach) and SCTHC003.03 (the downstream end of the listed reach). ADEQ conducted source identification monitoring of 3R Canyon and its major tributary Cox Gulch between 1999-2000. These events included additional sample points in upper 3R Canyon:

- SCUTH000.30 and SCTHC004.50 - natural background;
- SCTHC004.07 - below the 3R Mine complex, and;
- SCTHC004.01 - at the beginning of the intermittent reach.

Three additional sample points were established in the Cox Gulch segment:

- SCUCX000.01 - mouth of European Mine tributary;
- SCCXG001.04 - Cox Gulch just upstream from the mouth of the European Mine tributary, and;
- SCCXG000.85 - at the downstream end of the intermittent segment.

Due to lower-than-normal precipitation during this period, ADEQ was able to collect only a limited number of samples. (Figure 3 displays the ADEQ and USGS sampling locations; Tables 2A-2E display the measured data.)

4.2 General Sources

4.2.1 Natural Background

With respect to the definition of a natural background source, HydroGeoChem, Inc. (HGC) concluded:

> "... there are several areally-extensive zones of alteration and mineralization associated with the ore deposits in the subject watersheds. A field inspection verified that there are large portions of the subject watersheds containing naturally occurring disseminated pyrite and iron oxides due to weathering of pyrite." (HGC's Task 3 report, p. 4)

ADEQ staff selected natural background sampling sites: SCUTH000.30 (on the unnamed tributary north of the 3R Mine) and SCTHC004.50 in the south branch of 3R Canyon. Both sites are upstream of the 3R Mine and the area appears geologically similar to the rest of the subject reach and does not appear to have been disturbed by mining or other human activities.

The natural background concentrations used in calculating bankfull loads are the arithmetic average of measurements taken at sample points SCUTH000.30 and SCTHC004.50 multiplied by a flow extrapolated factor. Where sample results were reported as “not detected”, the concentration used was one-half of the detection limit. The flow extrapolation factors are calculated by the methodology explained in Appendix B.

H+ (pH) natural background concentration:

pH of 3.8 . 0.158 Fg/L H+ and a pH of 3.7 . 0.2 Fg/L H+

[(0.158 Fg/L + 0.2 Fg/L) / 2] x 0.173$_{\text{(flow extrapolation factor)}}$ = **0.031** Fg/L

Beryllium natural background concentration

dissolved: 0.25 Fg/L x0.446 $_{\text{(flow extrapolation factor)}}$ = **0.11 Fg/L**

total: 0.6 Fg/L x 0.443 $_{\text{(flow extrapolation factor)}}$ = **0.27 Fg/L**

Cadmium natural background concentration

dissolved: 0.5 Fg/L x 0.431 $_{\text{(flow extrapolation factor)}}$ **= 0.22 Fg/L**

total: 0.5 Fg/L x 0.638 $_{\text{(flow extrapolation factor)}}$ = **0.32 Fg/L**

Copper natural background concentration:

dissolved: 890 Fg/L x 0.791$_{\text{(flow extrapolation factor) =}}$ **704 Fg/L**

total: 885 Fg/L x 0.834 $_{\text{(flow extrapolation factor) =}}$ **738 Fg/L**

Zinc natural background concentration

dissolved: 38Fg/L x 0.579 $_{\text{(flow extrapolation factor)}}$ = **22 Fg/L**

total: 25 Fg/L x 0.597$_{\text{(flow extrapolation factor)}}$ = **15 Fg/L**

4.2.2 Adit drainage

Adit drainage was observed at two mines in the subject basin: the Ventura Mine group and the 3R Mine. While present, it is apparent that the adit drainage does not constitute a major source of pollutant loading in the subject basin. Neither discharge was sampled as part of this study.

C	The 3R Mine was observed on occasion to have a very low discharge from the mouth of the adit. This discharge was not observed to flow on the surface for more than approximately 10 meters. No data regarding sub-surface flow was collected.

C	The lowest (in elevation) adit of the Ventura Mine group has a continuous discharge that did not flow for more than 10 meters in the Cox Gulch stream channel before disappearing into the alluvium.

4.2.3 Mining residues

Mining residues are a significant source of pollutants and consist of three major categories of material:

C	Waste rock removed to gain access to the ore. (This material may or may not have leachable metals.)

C	Low grade ore waste that has leachable metals in quantities that were uneconomical to extract at the time of mining.

C	Mill tailings which are the finely ground waste after separation from the economically useful minerals. (This material may or may not have leachable metals.)

These materials are typically mixed (layered) in the same "dumps", dependent upon mine or mill activities at the time of dumping. The dumps are exposed to precipitation and are being slowly eroded and fed into the stream by runoff. ADEQ did not observe significant movement or erosion of this material after the low intensity (. two year) precipitation event that was sampled; however, gullies and rills were noticed during a sampling trip that occurred several days after a large localized precipitation event. It should be noted that these piles, which are in contact with the stream, are being constantly eroded and undercut creating a potential for collapse into the stream.

The USGS (in its study within the Sonoita Basin) came to the following conclusions about mining residue:

> The mine sites of the watershed typically include numerous adits and shafts, waste rock, and relic tailings dumps, and the larger sites typically have the remains of mills or other ore-handling fixtures, all resting on the steep, rocky banks of the stream. These sites release concentrations of metals in the "high metal" (high concentrations) category relative to a large range of mine types compiled from world literature (see Plumlee et al, 1993) (personal comm, Floyd Gray, USGS, 05/31/02)

4.2.4 Streambeds

Streambed sediments result from the wasting of mining residue piles and evaporative deposits from groundwater discharges which vary in composition as do the waste piles. Findings from the USGS investigation suggest that streambed sediments are the primary source of pollutant loading (personal comm, Floyd Gray, USGS, 05/31/02). Streambed sediments are not directly addressed by this phase of the TMDL due to a lack of data that can be used to associate sediment concentrations with water column concentrations at various discharges. Arizona does not currently have standards for sediments, but this loading source will be further characterized in a later phase of investigation.

4.3 Existing, Known Sources

Figure 4 displays the relative contributions by source. The sampling results shown in Tables 2A-2E and the modeling results shown in Tables 4 - 8 were used to support the following conclusions.

4.3.1 Three R (3R) Canyon

Evidence of mining activities in the basin above the 3R Mine is very limited and runoff from this area is considered natural background for purposes of this project.

The 3R Mine is a complex of shafts, adits, waste dumps, exposed cuts and a former mill. The mine complex is roughly Y-shaped, with the base pointing westerly and the two arms pointing northeasterly and southeasterly. The north arm contains an adit with occasional discharges but the flow disappears into the alluvium within 10 meters of the adit mouth. During dry weather conditions, no discharge was observed emanating from this adit. Both the north and south arms contain adits, shafts, cuts through mineralized material, and the north arm also contains a mostly demolished mill site and mill tailings piles. The junction of the Y contains a partially demolished ore tipple and the concrete pad of a compressor/engine building and other structures. The bottom leg of the Y is a cut through mineralized material and deposits (from runoff) of upstream materials. Currently, the mine is not in operation.

Approximately 800 meters below the 3R Mine is a low-flowing perennial spring of unknown origin feeding the intermittent segment of upper 3R Canyon. The intermittent flow is due to this spring discharge as bedrock-bottomed reaches upstream do not have flow except as runoff.

The approximately one mile segment of 3R Canyon between the spring and the mouth of Cox Gulch has a series of draws that feed into 3R Canyon and are dotted with the evidence of small mining operations (e.g., prospect pits, abandoned equipment), but no single potentially significant source of pollutant loading has been identified in this portion of the subject basin.

4.3.2 Cox Gulch

The Ventura Mine Group is at the head of Cox Gulch and is a complex of shafts and adits with multiple waste material piles and spills. There may have been mini-mills in the operation at some point. The mines are strung along an unnamed draw and waste material appears to have been used to fill and level portions of the draw where it has subsequently been cut by runoff. The lowest (in elevation) adit of the Ventura Group has a continuous acidic discharge. The trickle of flow was only occasionally observed to reach the stream channel and on the occasions that it did, disappeared into the alluvium within 10 meters.

In the approximately one mile between the Ventura Mine Group and the mouth of the tributary canyon containing the European Mine, there are several unidentified small mines. These are not in the streambed, but are located on the hillsides. Due to equipment malfunction, pH measurements were not made in this reach.

The European Mine is located in a canyon that has a few other small mines. Due to equipment malfunction, pH measurements were not made in this reach.

The confluence of the European Mine Canyon with Cox Gulch is above a bedrock-bottomed reach of Cox Gulch. The flow cuts the exposed bedrock along a geologic fault and forms a step-pool stream for approximately 250 meters. This bedrock-bottomed reach of the stream is the only intermittent reach of Cox Gulch; the rest of the system is ephemeral. The intermittent flow is most likely due to discharge from groundwater through the fault (spring) as bedrock-bottomed reaches upstream do not have flow except as runoff. The intermittent flow disappears into the alluvium within a few meters of the downstream end of the bedrock channel and does not reappear in the remainder of Cox Gulch. Cox Gulch is normally dry at its mouth.

4.4 Source Summary

Upper 3R Canyon, Cox Gulch and the tributaries are narrow steep-walled canyons with limited horizontal space available to support mining activity, yet there are many small mines throughout the basin which have a potential impact. During this first phase of the TMDL project, ADEQ was able to quantify contributions of the 3R Mine and the unnamed springs. Potentially significant contributions may come from stream sediments throughout the basin. ADEQ will attempt to quantify these loads during the second phase of the investigation.

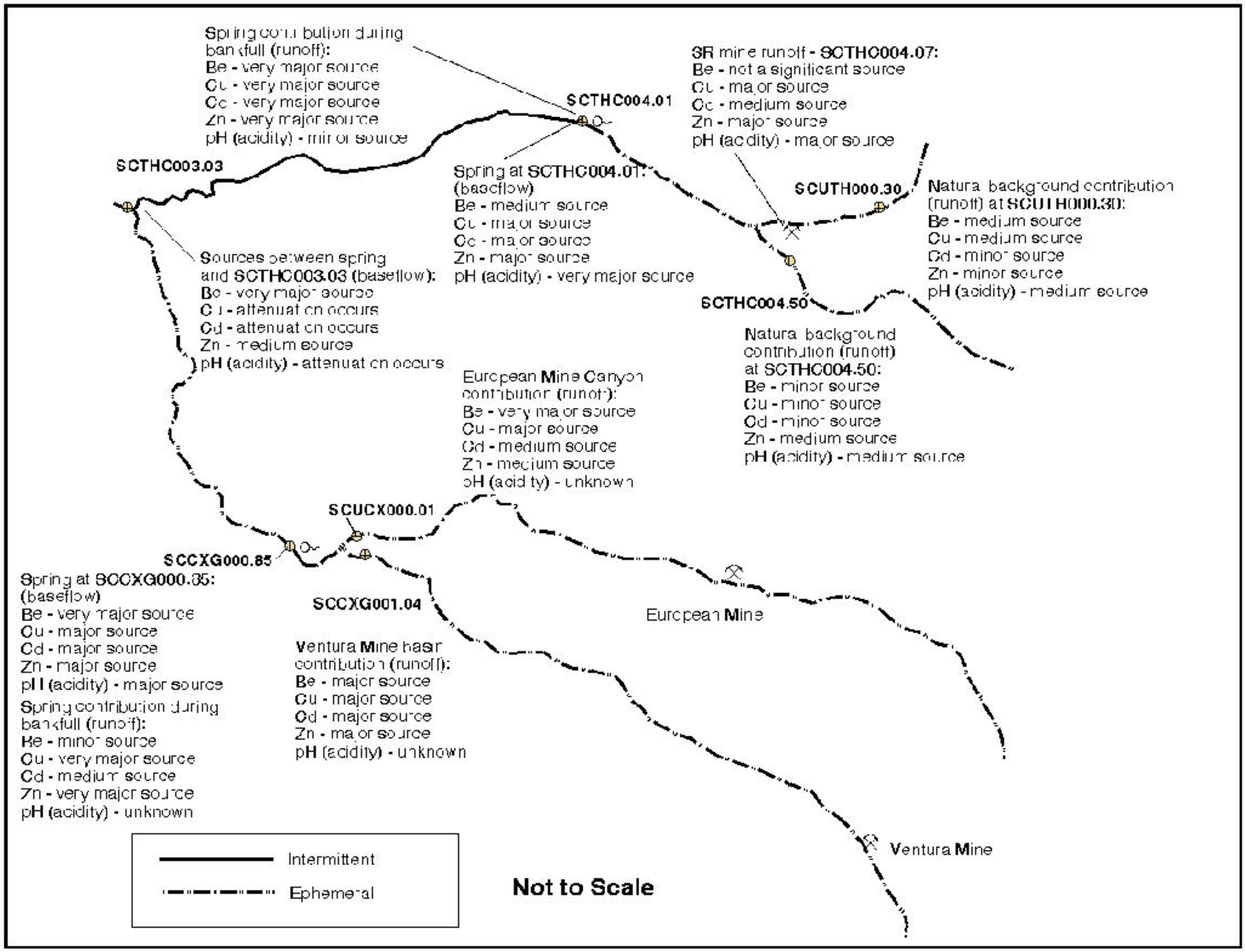


Figure 4 - 3R Canyon TMDL Project
Schematic
Relative Contributions by Source

Bob Scalamera
ADEQ/WQD/HSAS/TMDL Unit
02/11/03

5.0 LINKAGE ANALYSIS

5.1 Linkage of Sample Sites and Sources

Table 3 and Figure 4 display the linkage between each sample site (point of compliance) and the pollutant load sources corresponding to each point. Figure 4 also displays the relative significance of the load sources.

Table 3 Linkage of Sample Sites (Points of Compliance) and Sources

Site ID	Pollutant Sources
SCUTH000.30	Upstream from 3R Mine (north tributary): natural background sample as area appears geologically similar to the rest of the basin and undisturbed by mining
SCTHC004.50	Upstream from 3R Mine (south canyon): natural background sample as area appears geologically similar to the rest of the basin and undisturbed by mining
SCTHC004.07	Upstream from intermittent reach; downstream of 3R Mine: natural background and 3R Mine
SCTHC004.01	Upstream end of intermittent reach: groundwater (spring) + natural background + 3R Mine
SCCXG001.04	Cox Gulch, upstream from mouth of European Mine tributary (unnamed): natural background + headwaters + Ventura Mine
SCUCX000.01	European Mine tributary (unnamed): natural background + European Mine
SCCXG000.85	Cox Gulch, downstream from mouth of European Mine tributary (unnamed): natural background + groundwater (spring) + European and Ventura Mines
SCTHC003.03	Downstream from Cox Gulch mouth: subject basin combined

The pollutants of concern are linked in that all result from the action of water and oxygen on sulfide minerals in mining residues, streambed sediments, and naturally occurring mineral deposits which produces sulfuric acid. The acid acts to disassociate metals from the mineral matrix and make them available for transport in the dissolved form in the water column.

5.2 Critical Conditions

While the USGS study did not include sites usable in the 3R Canyon TMDL, ADEQ believes the conclusions from the investigations into Alum Gulch and Harshaw Creek accurately characterize the factors critical to loading in 3R Canyon as well.

> Periodically, almost seasonally, release of waste rock into the streams were observed with the subsequent release of metals to the water column. This metal release by waste rock movement is a significant component in low volume desert waterways.
>
> Waste material captured in the stream during storms is transported downstream and deposited preferentially in areas of shallow gradient where the velocity and suspended load capacity of the stream is diminished. The process by which storm water is degraded appears to be via interaction with reactive detritus (e.g. sulfide-bearing siliceous waste rock, sulfate salts) from waste piles and from interaction with highly soluble salts accumulated in stream-bed sediment via evaporation. By the combined actions of these processes the acid generating potential of downstream areas typically resembles that of upstream mine sites and thus the water chemistry changes little during transport. Therefore these stream

segments have the highest potential for the release of metals into the watershed.

Metal concentrations from water and sediment samples collected downstream from dump sites by the USGS during storm runoff are substantially higher than those measured in gullies and sheet flow above the primary streambed. The USGS has concluded that mine dump erosion and the accumulation of evaporative salts from acidic, metal-enriched discharge from abandoned mine sites are the largest contributors to degraded streamflow during storm events (personal comm, Floyd Gray, USGS, 05/31/02).

This TMDL provides for attainment of water quality standards under all flow regimes by using selected critical flow and/or loading conditions as critical modeling scenarios. Loads may be different within a hydrologic event (i.e., "first flush" versus later samples) and between sample events. As previously mentioned, the USGS considers sediment, including evaporative deposits, to be the major sources of pollutant load and contend that flows through the sediment and evaporative salt deposits will trigger loading, regardless of season.

The ADEQ-chosen critical flows to model were the 2-year, 24-hour event (approximately bankfull) and baseflow. The model is capable of calculating loads at flows other than these critical flows due to the use of the extrapolation factors. Input of the selected flow into the model will result in loads and TMDLs calculated for the selected flow. ADEQ collected samples/measurements in the subject streams during baseflow conditions and, in limited quantities, during higher flows which were used to calculate extrapolation factors as explained in Appendix B. At flows ranging from zero to bankflow, the loads calculated using baseflow discharges apply; at flows equal to and greater than bankfull, the loads calculated using bankfull discharges apply.

As mentioned in the Hydrology section, the baseflow portion of the stream is solely derived from spring discharges. (Note: Baseflow is not be further defined as the commonly used design flow of "7Q10 flow" because of the lack of the necessary gage data and, in the case of an ephemeral stream, 7Q10 flows tend to equal zero.)

Because flow interaction with sediment is considered to be the primary source of loading (as confirmed by the USGS), bankfull was also chosen as a critical modeling condition as this is the flow during which the most sediment disturbance or movement occurs over time (Leopold, 1978). In Arizona, the bankfull event generally occurs at approximately the 1.1 to 1.8 year return interval; channels in mountainous regions (such as the subject stream) are close to the 1.4 year return interval (Moody, 1999). The 2 year return interval precipitation event is the closest to 1.4 year with sufficient data available to feed a hydrologic model. (Note: Bankfull field estimations are based upon field observations and measurements in "Regional Relationships For Bankfull Stage in Natural Channels of Central and Southern Arizona", Northern Arizona University, College of Engineering and Technology, Moody, T. O. & W. Odem, February, 1999.)

6.0 LOAD CALCULATIONS AND TMDL

6.1 Model Considerations

6.1.1 Data Sources and Limitations

Because there are no rain gauges or flow gauges within the subject reach of 3R Canyon, historic data was not available for model calibration. Additionally, drought conditions greatly reduced the opportunity for sample collection. ADEQ did measure stream cross-sections at or near many of the sample points for purposes of hydrologic model setup.

Because of the limited amount of precipitation, flow and water quality data, load modeling requires a number of assumptions be made. For example, assumptions such as initial loss and runoff transformation can be generalized/estimated as they have less impact on model outcomes. These assumptions are not unusual in water quality analysis, regulation and TMDL development. This lack of data is one of the reasons ADEQ considers this project to be a first phase of the TMDL.

In HGC's Model Selection Report, a succinct analysis of data limitations is made.

> With respect to runoff estimation, there is a good geomorphologic basis for constructing a runoff model, but calibration of the model will be difficult due to the lack of runoff hydrographs for measured precipitation events. The ephemeral nature of most flows and the lack of continuous runoff data argues for using an event-based model rather than a continuous model. The need for a simple method of rainfall runoff estimation is indicated by the inability to calibrate the model.
>
> To model mass loading, the water quality of runoff will need to be generalized to large areas and considered steady with respect to time and discharge. The limited spatial coverage of the water quality data and the lack of information on sediment dictates that chemical processes that may potentially transfer constituents between different phases and sources cannot be considered, and that simple mixing will have to be assumed. These factors indicate that a relatively simple method of tracking the mass balance such as a spreadsheet program would be sufficient. (HGC's Task 3 report, p. E-2)

HGC concluded the Model Findings Report by stating,

> Given the ephemeral nature of the subject watersheds and the limited flow and water quality data available, the runoff estimates and loading calculations reported herein are adequate as a first approximation for making water quality management decisions. (HGC's Task 4 report, p. 36)

6.1.2 Conceptual Model

The following is excerpted from Task 3 - Report of Model Selection Findings.

> "*Based on the conceptual model and availability of data, an appropriate model for the Sonoita Basin simulates surface runoff and baseflow from a rural area at a watershed and subbasin scale, performs event-based simulations, requires no calibration, and allows prescription of runoff concentrations at a subbasin scale (e.g., as a function of land use) for load calculation.*
>
> *Guidance for model selection is provided in the EPA's Compendium of Tools for Watershed Assessment and TMDL Development (EPA, 1997). Watershed-scale*

loading models described by EPA (1997) are the most appropriate for Sonoita Basin project but were generally more complex than warranted due to the lack of calibration data. Based on the review of watershed-scale loading models and the constraints on modeling due to data availability, the most appropriate method to evaluate loading was determined to be use of the rainfall-runoff model HEC-HMS developed by the United States Corps of Engineers (sic) *to estimate runoff and a spreadsheet calculation procedure to estimate subreach loading.*" (HGC's Task 3 report, p. E-2)

6.1.3 Flows

Event based rainfall-runoff simulations were performed using HEC-HMS. Precipitation events (2 year, 24 hour rainfalls) were determined from the isopluvial contour maps in NOAA (1973). Based upon field observations, this high-frequency, low volume rainfall is the most likely to have produced the conditions under which existing discharge and water quality measurements were made. The other critical flow, baseflow, used ADEQ-measured data.

"*The rainfall runoff model was constructed to represent the subject watershed to the best degree possible, although the accuracy of the predicted runoff rates and volumes cannot be quantitatively determined because there are no rainfall runoff measurements of actual storms with which to calibrate and validate the model.*" (HGC's Task 4 report)

6.1.4 Loads

"*Well mixed conditions and non-reactive transport of hydrogen ions and metals would be assumed so that resulting concentrations could be calculated by simple mixing. This approach to loading analysis is based on standard principles of load estimation.*" (HGC's Task 3 report, p. 22)

The HEC-HMS estimated stream flow and ADEQ measured baseflow were combined with the measured and estimated pollutant concentrations at various locations in a Quattro Pro® spreadsheet (Tables 4 - 8) to calculate loading estimates at each target site.

6.1.5 Modeling Scenarios

Several different flow scenarios were modeled to consider possible extremes. These scenarios were coupled with a synthetic rainfall distribution that is likely to occur in the Sonoita Basin.

The high-frequency precipitation events, the 2-, 5-, 10-year, and 24-hour rainfalls, were determined using isopluvial contour maps from NOAA (1973). High frequency, low volume rainfalls are the most likely to have produced the conditions during which existing discharge and water quality measurements were made. A low frequency event, the 100-year 24-hour rainfall was also evaluated. (From HGC's Task 3 report, p. E-3)

Because the critical condition for loading is flow dependent, the 2-year scenario and a baseflow scenario, developed by ADEQ, were used to develop load scenarios.

6.1.6 Calculation of Flow-extrapolated Concentrations

Due to the ephemeral nature of the subject streams and the lack of precipitation during the period of the investigation, a limited number of samples were collected in the upper 3R Canyon basin. A number of the samples were measurements of streamflow resulting from groundwater discharge. Generally, the measurements of runoff were less than bankfull. Therefore, ADEQ determined a means of extrapolating the limited measured concentrations and flows was needed in order to model bankfull loads. The method for determining these extrapolation factors is described below and explained in detail with examples in Appendix B.

Results from the monitoring point (SCTHC003.03, downstream at bottom end of subject reach) with measurements under both high and low flow conditions were used to calculate a "bankfull extrapolation factor". The bankfull concentrations calculated using the flow-weighted extrapolation factor were tested against the measured values. The methodology for calculating the flow extrapolation factors is detailed in Appendix B.

6.2 Load Capacity

The measured and modeled concentrations are used to calculate corresponding loads of the 303[d]-listed pollutants. These loads are based on the modeled hardness and flow.

Tables 4A - 4K display the Load Capacity values calculated according to the formula below and show the 20% explicit margin of safety (see section 6.3) which is based on the load capacity:

Load Capacity = 0.0024465 x Flow x Numeric Target (standard)

The loads and other values necessary to calculate load allocations and TMDLs (Tables 4 -6) were calculated using the following:

The value 0.0024465 is an units conversion factor to get from Fg/L and cubic feet per second (cfs) to kg/day:

[*1.0 x* 10^{-9} *kg/Fg @ 28.316 L/*ft^3 *@ 86,400 sec/day] @ (conc) Fg/L @ (flow)* ft^3*/sec @ concentration extrapolation factor*

which works out to:

[0.0024465] @ conc @ flow @ concentration extrapolation factor = ***load in kg/day***

CALCULATING LOAD CAPACITY
TABLES 4A through 4K

<u>Abbreviations to tables:</u>
NNS = no numeric standard applicable
N/A = not applicable

Table 4A Natural Background (runoff)
Sample point: SCUTH000.30
Bankfull discharge = 5.6 cfs

Parameter	Hardness (mg/L)	WQS (Fg/L)	Load Capacity (kg/day)	MOS (kg/day)
Be (diss)	N/A	NNS	N/A	N/A
Be (total)	N/A	2,800	38	7.7
Cd (diss)	25	14	0.2	0.039
Cd (total)	N/A	50	0.69	0.14
Cu (diss)	25	6.3	0.086	0.017
Cu (total)	N/A	500	6.9	1.4
Zn (diss)	25	344	4.7	0.94
Zn (total)	N/A	25,000	343	69
H+ (pH)	N/A	0.00032	4.4E-06	9E-07

Table 4B Natural Background (runoff)
Sample point: SCTHC004.50
Bankfull discharge = 4.0 cfs

Parameter	Hardness (mg/L)	WQS (Fg/L)	Load Capacity (kg/day)	MOS (kg/day)
Be (diss)	N/A	NNS	N/A	N/A
Be (total)	N/A	2,800	27	5.5
Cd (diss)	25	14	0.14	0.028
Cd (total)	N/A	50	0.49	0.098
Cu (diss)	25	6.3	0.062	0.012
Cu (total)	N/A	500	4.9	0.98
Zn (diss)	25	344	3.4	0.67
Zn (total)	N/A	25,000	245	49
H+ (pH)	N/A	0.00032	3.1E-06	6E-07

Table 4C 3R Mine plus natural background (runoff)
Sample point: SCTHC004.07
Bankfull discharge = 13.7 cfs

Parameter	Hardness (mg/L)	WQS (Fg/L)	Load Capacity (kg/day)	MOS (kg/day)
Be (diss)	N/A	NNS	N/A	N/A
Be (total)	N/A	2,800	94	19
Cd (diss)	25	14	0.48	0.096
Cd (total)	N/A	50	1.7	0.34
Cu (diss)	25	6.3	0.21	0.042
Cu (total)	N/A	500	17	3.4
Zn (diss)	25	344	12	2.3
Zn (total)	N/A	25,000	838	168
H+ (pH)	N/A	0.00032	1.1E-05	2.1E-06

Table 4D 3R Spring (point source)
Sample point: SCTHC004.01
Baseflow discharge = 0.001 cfs

Parameter	Hardness (mg/L)	WQS (Fg/L)	Load Capacity (kg/day)	MOS (kg/day)
Be (diss)	N/A	5.3	1.3E-05	2.6E-06
Be (total)	N/A	1,130	0.0028	0.00055
Cd (diss)	53	1.4	3.4E-06	7E-07
Cd (total)	N/A	50	0.00012	2.4E-05
Cu (diss)	53	5.2	1.3E-05	2.5E-06
Cu (total)	N/A	500	0.0012	0.00024
Zn (diss)	53	68	0.00017	3.4E-05
Zn (total)	N/A	25,000	0.061	0.012
H+ (pH)	N/A	0.00032	1E-09	0

Table 4E 3R spring plus upstream sources (runoff)
Sample point: SCTHC004.01
Bankfull discharge = 14.1 cfs

Parameter	Hardness (mg/L)	WQS (Fg/L)	Load Capacity (kg/day)	MOS (kg/day)
Be (diss)	N/A	5.3	0.18	0.037
Be (total)	N/A	1,130	39	7.8
Cd (diss)	38	1.1	0.038	0.0075
Cd (total)	N/A	50	1.7	0.34
Cu (diss)	38	3.9	0.14	0.027
Cu (total)	N/A	500	17	3.4
Zn (diss)	38	52	1.8	0.36
Zn (total)	N/A	25,000	862	172
H+ (pH)	N/A	0.00032	1.1E-05	2.2E-06

Table 4F Cox Gulch - Ventura Mine basin (Ventura Mine and other unnamed mines) (nonpoint sources) - Sample point: SCCXG001.04
Bankfull discharge = 6.1 cfs

Parameter	Hardness (mg/L)	WQS (Fg/L)	Load Capacity (kg/day)	MOS (kg/day)
Be (diss)	N/A	NNS	N/A	N/A
Be (total)	N/A	2,800	42	8.4
Cd (diss)	120	79	1.2	0.23
Cd (total)	N/A	50	0.75	0.15
Cu (diss)	120	28	0.41	0.082
Cu (total)	N/A	500	7.5	1.5
Zn (diss)	120	1,298	19	3.9
Zn (total)	N/A	25,000	373	75
H+ (pH)	N/A	0.00032	4.8E-06	1E-06

Table 4G Cox Gulch - European Mine basin (European Mine and other unnamed mines) (nonpoint sources) - Sample point: SCCXG000.01
Bankfull discharge = 10.8 cfs

Parameter	Hardness (mg/L)	WQS (Fg/L)	Load Capacity (kg/day)	MOS (kg/day)
Be (diss)	N/A	NNS	N/A	N/A
Be (total)	N/A	2,800	74	15
Cd (diss)	78	49	1.3	0.26
Cd (total)	N/A	50	1.3	0.26
Cu (diss)	78	18	0.49	0.097
Cu (total)	N/A	500	13	2.6
Zn (diss)	78	901	24	4.8
Zn (total)	N/A	25,000	661	132
H+ (pH)	N/A	0.00032	8.5E-06	1.7E-06

Table 4H Intermittent reach of Cox Gulch (point source)
Sample point: SCCXG000.85

Baseflow discharge = 0.001 cfs

Parameter	Hardness (mg/L)	WQS (Fg/L)	Load Capacity (kg/day)	MOS (kg/day)
Be (diss)	N/A	5.3	1.3E-05	2.6E-06
Be (total)	N/A	1,130	0.0028	0.00055
Cd (diss)	400	6.2	1.5E-05	3E-06
Cd (total)	N/A	50	0.00012	0.000024
Cu (diss)	400	29	7.2E-05	1.4E-05
Cu (total)	N/A	500	0.0012	0.00024
Zn (diss)	400	379	0.00093	0.00019
Zn (total)	N/A	25,000	0.061	0.012
H+ (pH)	N/A	0.00032	1E-09	0

Table 4I Intermittent reach of Cox Gulch (runoff)
Sample point: SCCXG00.85
Bankfull discharge = 17.1 cfs

Parameter	Hardness (mg/L)	WQS (Fg/L)	Load Capacity (kg/day)	MOS (kg/day)
Be (diss)	N/A	5.3	0.22	0.044
Be (total)	N/A	1,130	47	9.5
Cd (diss)	182	3.5	0.15	0.029
Cd (total)	N/A	50	2.1	0.42
Cu (diss)	182	15	0.62	0.12
Cu (total)	N/A	500	21	4.2
Zn (diss)	182	195	8.1	1.6
Zn (total)	N/A	25,000	1046	209
H+ (pH)	N/A	0.00032	1.3E-05	2.7E-06

Table 4J 3R Canyon intermittent reach (nonpoint source)
Sample point: SCTHC003.03
Baseflow discharge = 0.11 cfs

Parameter	Hardness (mg/L)	WQS (Fg/L)	Load Capacity (kg/day)	MOS (kg/day)
Be (diss)	N/A	5.3	0.0014	0.00029
Be (total)	N/A	1,130	0.3	0.061
Cd (diss)	291	4.9	0.0013	0.00026
Cd (total)	N/A	50	0.013	0.0027
Cu (diss)	291	22	0.006	0.0012
Cu (total)	N/A	500	0.13	0.027
Zn (diss)	291	290	0.078	0.016
Zn (total)	N/A	25,000	6.7	1.3
H+ (pH)	N/A	0.00032	8.6E-08	0

Table 4K 3R Canyon, Cox Gulch (all upstream sources) (runoff)
Sample point: SCTHC003.03
Bankfull discharge = 42.5 cfs

Parameter	Hardness (mg/L)	WQS (Fg/L)	Load Capacity (kg/day)	MOS (kg/day)
Be (diss)	N/A	5.3	0.55	0.11
Be (total)	N/A	1,130	117	23
Cd (diss)	206	3.8	0.4	0.079
Cd (total)	N/A	50	5.2	1
Cu (diss)	206	17	1.7	0.35
Cu (total)	N/A	500	52	10
Zn (diss)	206	216	22	4.5
Zn (total)	N/A	25,000	2,599	520
H+ (pH)	N/A	0.00032	3.3E-05	6.7E-06

CALCULATING EXISTING LOADS
TABLES 5A through 5K

Tables 5A - 5K display the Existing Load and its components: Natural Background and Human-caused calculated according to the formula:

> **Existing Load** = 0.0024465 (unit conversion factor) x Flow x Existing Concentration
> **Natural Background Loading** = 0.0024465 (unit conversion factor) x Flow x Natural Background Concentration
> **Human-caused Load** = Existing Load - Natural Background Loading

Note: Loads resulting from runoff include a natural background load.

Table 5A Natural Background (runoff) - existing load = natural background
Sample point: SCUTH000.30
Bankfull discharge = 5.6 cfs

Parameter	Existing Conc (Fg/L)	Existing Load (kg/day)	Nat Back Conc (Fg/L)	Nat Back Load (kg/day)	Human-Caused Load (kg/day)
Be (diss)	0.11	0.0015	0.11	0.0015	NA
Be (total)	0.31	0.0042	0.31	0.0042	NA
Cd (diss)	0.22	0.003	0.22	0.003	NA
Cd (total)	0.32	0.0044	0.32	0.0044	NA
Cu (diss)	1,107	15	1,107	15	NA
Cu (total)	1,168	16	1,168	16	NA
Zn (diss)	14	0.19	14	0.19	NA
Zn (total)	15	0.21	15	0.21	NA
H+ (pH)	0.027	0.00037	0.027	0.00037	NA

Table 5B Natural Background (runoff) - existing load = natural background
Sample point: SCTHC004.50
Bankfull discharge = 4.0 cfs

Parameter	Existing Conc (Fg/L)	Existing Load (kg/day)	Nat Back Conc (Fg/L)	Nat Back Load (kg/day)	Human-Caused Load (kg/day)
Be (diss)	0.11	0.0011	0.11	0.0011	NA
Be (total)	0.22	0.0022	0.22	0.0022	NA
Cd (diss)	0.22	0.0022	0.22	0.0022	NA
Cd (total)	0.32	0.0031	0.32	0.0031	NA
Cu (diss)	301	2.9	301	2.9	NA
Cu (total)	309	3	309	3	NA
Zn (diss)	30	0.29	30	0.29	NA
Zn (total)	15	0.15	15	0.15	NA
H+ (pH)	0.035	0.00034	0.035	0.00034	NA

Table 5C 3RMine plus natural background (runoff)
Sample point: SCTHC004.07

Bankfull discharge = 13.7 cfs

Parameter	Existing Conc (Fg/L)	Existing Load (kg/day)	Nat Back Conc (Fg/L)	Nat Back Load (kg/day)	Human-Caused Load (kg/day)
Be (diss)	0.11	0.0037	0.11	0.0037	0
Be (total)	0.11	0.0037	0.265	0.0037	0
Cd (diss)	0.69	0.023	0.22	0.00074	0.016
Cd (total)	1.1	0.037	0.32	0.011	0.026
Cu (diss)	5,695	191	704	24	167
Cu (total)	6,422	215	738.5	25	190
Zn (diss)	64	2.1	22	0.74	1.4
Zn (total)	56	1.9	15	0.5	1.4
H+ (pH)	0.055	0.0018	0.031	0.001	0.0008

Table 5D 3R Spring (point source)
Sample point: SCTHC004.01
Baseflow discharge = 0.001 cfs
Note: Existing loads cannot be further classified as natural or human at this discharge.

Parameter	Existing Conc (Fg/L)	Existing Load (kg/day)
Be (diss)	2.2	5.4E-06
Be (total)	2.7	6.6E-06
Cd (diss)	64	0.00016
Cd (total)	58	0.00014
Cu (diss)	60,250	0.15
Cu (total)	58,000	0.14
Zn (diss)	1,563	0.0038
Zn (total)	1,557	0.0038
H+ (pH)	1.1	2.7E-06

Table 5E 3R spring plus upstream sources (runoff)
Sample point: SCTHC004.01
Bankfull discharge = 14.1 cfs

Parameter	Existing Conc (Fg/L)	Existing Load (kg/day)	Nat Back Conc (Fg/L)	Nat Back Load (kg/day)	Human-Caused Load (kg/day)
Be (diss)	0.89	0.031	0.11	0.0038	0.027
Be (total)	2.3	0.079	0.265	0.0091	0.07
Cd (diss)	27	0.93	0.22	0.0076	0.92
Cd (total)	37	1.3	0.32	0.011	1.3
Cu (diss)	47,658	1,644	704	24	1,620
Cu (total)	48,372	1,669	738.5	25	1,643
Zn (diss)	905	31	22	0.76	30
Zn (total)	929	32	15	0.52	32
H+ (pH)	0.2	0.0069	0.031	0.0011	0.0058

Table 5F Cox Gulch - Ventura Mine basin (Ventura Mine and other unnamed mines) (nonpoint sources) (runoff)
Sample point: SCCXG001.04
Bankfull discharge = 6.1 cfs
Note: No H+ measurement taken at this location.

Parameter	Existing Conc (Fg/L)	Existing Load (kg/day)	Nat Back Conc (Fg/L)	Nat Back Load (kg/day)	Human-Caused Load (kg/day)
Be (diss)	3.7	0.055	0.11	0.0016	0
Be (total)	4.1	0.061	0.265	0.004	0.057
Cd (diss)	11	0.16	0.22	0.0033	0.16
Cd (total)	22	0.33	0.32	0.005	0.32
Cu (diss)	1,848	28	704	11	17
Cu (total)	1,697	25	738.5	11	14
Zn (diss)	2,331	35	22	0.33	34
Zn (total)	2,274	34	15	0.22	34
H+ (pH)	N/A	N/A	N/A	N/A	N/A

Table 5G Cox Gulch - European Mine basin (European Mine and other unnamed mines) (nonpoint sources) -Sample point: SCCXG000.01
Bankfull discharge = 10.8 cfs
Note: No H+ measurement taken at this location.

Parameter	Existing Conc (Fg/L)	Existing Load (kg/day)	Nat Back Conc (Fg/L)	Nat Back Load (kg/day)	Human-Caused Load (kg/day)
Be (diss)	3.7	0.098	0.11	0.0029	0
Be (total)	4	0.11	0.265	0.007	0.099
Cd (diss)	6	0.16	0.22	0.0058	0.15
Cd (total)	7.7	0.2	0.32	0.0085	0.19
Cu (diss)	1,756	46	704	19	28
Cu (total)	1,482	39	738.5	20	20
Zn (diss)	1,146	30	22	0.58	30
Zn (total)	910	24	15	0.4	24
H+ (pH)	N/A	N/A	N/A	N/A	N/A

Table 5H Intermittent reach of Cox Gulch (point source)
Sample point: SCCXG000.85
Baseflow discharge = 0.001 cfs
Note: Existing loads cannot be further classified as natural or human at this discharge.

Parameter	Existing Conc (Fg/L)	Existing Load (kg/day)
Be (diss)	7.6	1.9E-05
Be (total)	10	2.4E-05
Cd (diss)	38	9.3E-05
Cd (total)	54	0.00013
Cu (diss)	13,100	0.032
Cu (total)	13,300	0.033
Zn (diss)	7,100	0.017
Zn (total)	7,600	0.019
H+ (pH)	0.5	1.2E-06

Table 5I Intermittent reach of Cox Gulch (runoff)
Sample point: SCCXG00.85
Bankfull discharge = 17.1 cfs

Parameter	Existing Conc (Fg/L)	Existing Load (kg/day)	Nat Back Conc (Fg/L)	Nat Back Load (kg/day)	Human-Caused Load (kg/day)
Be (diss)	4.2	0.18	0.11	0.0046	0.17
Be (total)	5.6	0.23	0.265	0.011	0.22
Cd (diss)	16	0.67	0.22	0.0092	0.66
Cd (total)	34	1.4	0.32	0.013	1.4
Cu (diss)	3,026	127	704	29	97
Cu (total)	2,594	109	738.5	31	78
Zn (diss)	2,805	117	22	0.92	116
Zn (total)	2,880	120	15	0.63	120
H+ (pH)	0.087	0.0036	0.031	0.0013	0.0023

Table 5J 3R Canyon intermittent reach (nonpoint source)
Sample point: SCTHC003.03
Baseflow discharge = 0.11 cfs
Note: No natural background load applicable at this location at this discharge.

Parameter	Existing Conc (Fg/L)	Existing Load (kg/day)	Nat Back Conc (Fg/L)	Nat Back Load (kg/day)	Human-Caused Load (kg/day)
Be (diss)	9	0.0024	N/A	N/A	0.0024
Be (total)	8	0.0022	N/A	N/A	0.0022
Cd (diss)	19	0.0051	N/A	N/A	0.0051
Cd (total)	24	0.0065	N/A	N/A	0.0065
Cu (diss)	24,350	6.6	N/A	N/A	6.6
Cu (total)	24,650	6.6	N/A	N/A	6.6
Zn (diss)	2,965	0.8	N/A	N/A	0.8
Zn (total)	3,760	1	N/A	N/A	1
H+ (pH)	0.4	0.00011	N/A	N/A	0.00011

Table 5K 3R Canyon, Cox Gulch (all upstream sources) (runoff)
Sample point: SCTHC003.03
Bankfull discharge = 42.5 cfs

Parameter	Existing Conc (Fg/L)	Existing Load (kg/day)	Nat Back Conc (Fg/L)	Nat Back Load (kg/day)	Human-Caused Load (kg/day)
Be (diss)	4	0.42	0.11	0.011	0.4
Be (total)	3.5	0.36	0.265	0.028	0.34
Cd (diss)	8.2	0.85	0.22	0.023	0.83
Cd (total)	15	1.6	0.32	0.033	1.5
Cu (diss)	19,261	2,003	704	73	1,929
Cu (total)	20,558	2,138	738.5	77	2,061
Zn (diss)	1,717	179	22	2.3	176
Zn (total)	2,245	233	15	1.6	232
H+ (pH)	0.13	0.014	0.031	0.0032	0.01

6.3 Margin of Safety

6.3.1 Explicit Margin of Safety

This TMDL has been calculated based on real loads at baseflow and simulated loads at a higher flow with a return interval of two years.

The precision of measurement of the parameters of concern is plus or minus 5% (personal comm, State Laboratory, Arizona Department of Health Services). An explicit margin of safety of 5% was applied to the TMDL to account for this error.

An additional explicit margin of safety of 15% was applied to account for:

C The lack of characterization of many of the minor sources in the subject basin;

C The potential for unidentified sources to contribute pollutant loads or identified sources to provide larger loads than anticipated; and

C The modeling for the project assumes homogeneous rainfall across the entire subject basin. However, precipitation events can occur in portions of the watershed with other portions receiving none and thereby resulting in runoff patterns and stream discharges different from those modeled.

The total explicit margin of safety used is 20% of the load capacity.

6.3.2 Implicit Margin of Safety

A non-quantifiable implicit margin of safety was applied through:

C Not allocating additional loading when capacity was available. When the existing load for a stream segment was less than the load capacity; i.e., standards are not being exceeded, instead of using the difference between load capacity and existing loading as additional allowable load, ADEQ chose not to allow any additional loading. This was done for several reasons:

    < Even if one or more segments meet standards, the stream reach as a whole does not necessarily meet standards; therefore, additional loading was not allocated.

    < To allow for non-quantifiable errors in modeling methodology.

    < To allow for future sources. This allowance is not required by law, but neither is it prohibited. (Future sources are most likely to take the form of additional loading caused by the exposure of "fresh" mineralized material to runoff.)

C Use of conservative modeling assumptions, for example:

    < "*The assumption of steady concentrations may overestimate loading because most chemical analyses are for samples collected at relatively low flows, and thus potentially represent higher concentrations, compared to the event average flows used to calculate loading.*" (HGC's Task 4 report, p. 35)

- The model assumes conservative mixing and does not account for physical and chemical processes occurring in-stream that may reduce concentrations between sample points.

6.4 Allocations and TMDL

The in-stream water quality in the subject waterbodies is such that loads need to be reduced in order to meet standards. The following TMDLs and associated allocations are set at levels adequate to result in the attainment of applicable water quality standards.

6.4.1 TMDL Calculations

The TMDL is represented by the a mathematical equation:

TMDL = ΣWLA + ΣLA + MOS + Natural Background, where:

WLA is the wasteload allocation consisting of loads from point sources (not used in this phase of the TMDL),

LA is the load allocation consisting of non-point source loads, and

MOS is a Margin of Safety which serves to address uncertainties in the analysis and the natural system.

In order to increase clarity, ADEQ has chosen to break out **Natural Background** from the LA as the loading due to natural background sources.

There are currently no NPDES-permitted point sources identified in the subject watershed; however, ADEQ plans to conduct a detailed survey to determine if any point sources exist as part of a later phase of the subject TMDL. The final TMDLs set for the pollutants in the listed portion of 3R Canyon will not change solely if a source currently considered to be nonpoint source is later determined to be a point source. With respect to the TMDL equation, the only change that would be made in this event would be the movement of a load from the load allocation column to the wasteload allocation column.

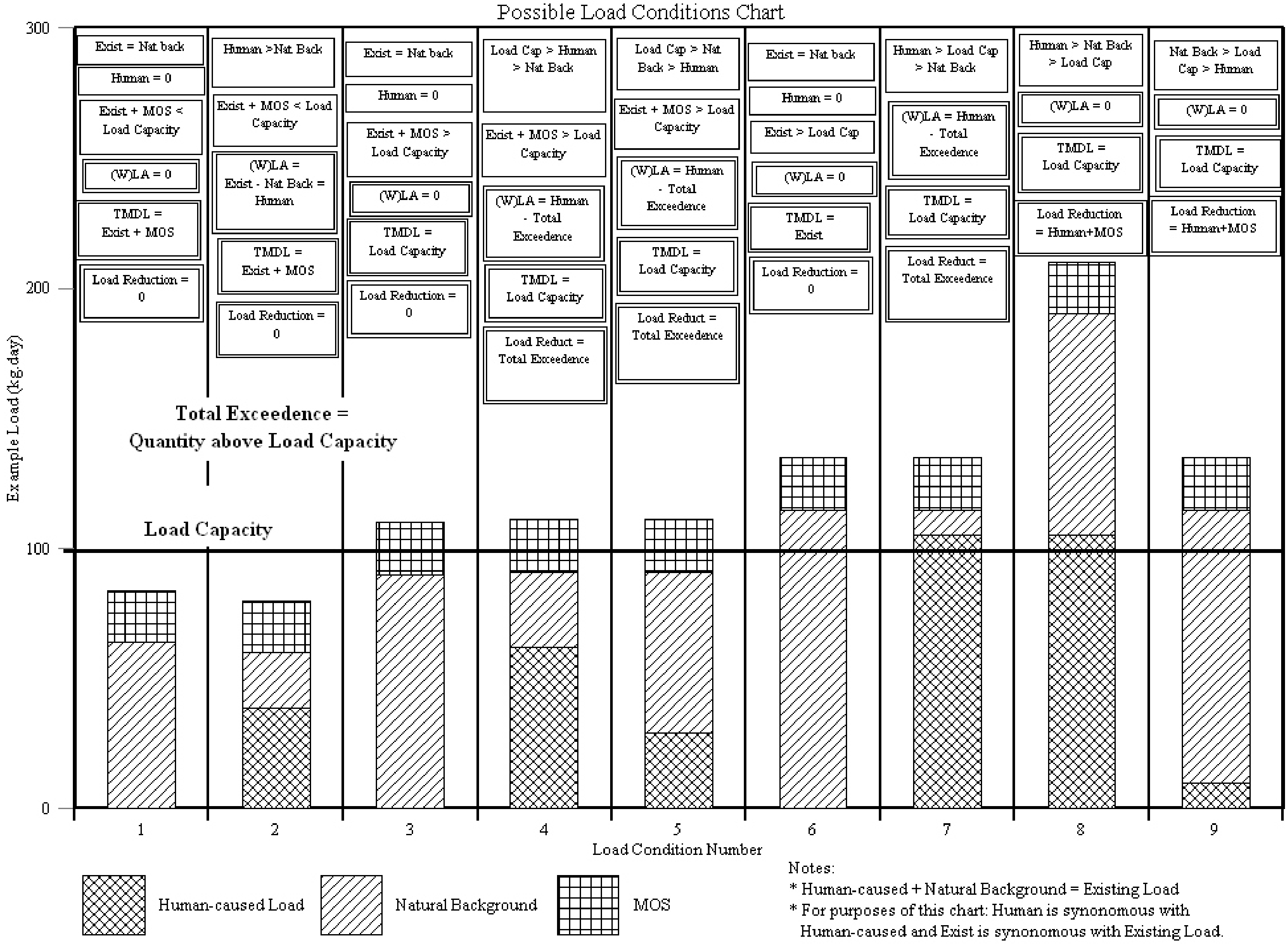
In this first phase of the TMDL, loads at each sample point include the upstream loads. In later phases of this TMDL, ADEQ may elect to break out the upstream load from each load when enough data has been collected to allow more accurate accounting for in-stream physical and chemical processes such as: dilution; reactions with other inputs; precipitation; binding or reacting with sediments. Additionally, load allocations might be calculated for discrete sources.

The application of the extrapolation factor to the natural background measurements is most accurate at the point of collection. When the natural background load calculated at the point of collection is applied to other sample points, apparent inconsistencies in mass balance may occur, such as the measured load being less than the estimated background load. This occurs because the model assumes conservative mixing and does not account for physical and chemical processes that reduce in-stream concentrations between the background and the downstream sample points. These processes, which include dilution with discharging ground water or other surface flows, precipitation of metal hydroxides from streamflow, and metal adsorption to stream sediment, are too complicated to be practically modeled at the watershed scale without detailed flow measurements and chemical information for water and sediment.

ADEQ does not consider this prima facie evidence of a need for site specific standards. In later phases of this TMDL, ADEQ will collect necessary data to further characterize natural background.

Tables 6A - 6K summarize the values needed to calculate the load allocations and display the load allocations, TMDLs and the load reductions necessary to meet the TMDLs. The calculation of the load allocations are completed in accordance with the conditions displayed in Figure 5. The “load condition” column in tables 6A - 6K corresponds to the numbers along the bottom of Figure 5. Unless otherwise specified, all the tables are ordered by source. All units are kg/day.

Figure 5
Possible Load Conditions Chart



Notes:
* Human-caused + Natural Background = Existing Load
* For purposes of this chart: Human is synonomous with Human-caused and Exist is synonomous with Existing Load.

CALCULATING LOAD ALLOCATIONS AND TMDLs
TABLES 6A through 6K

Table 6A Natural Background (runoff)
Sample point: SCUTH000.30
Bankfull discharge = 5.6 cfs

Parameter	Load Cond (Fig. 5)	Load Capacity (kg/day)	MOS (kg/day)	Nat Back Load (kg/day)	Human-Caused Load (kg/day)	Load Allocation (kg/day)	TMDL (kg/day)	Load Reduction (kg/day)
Be (diss)	N/A	NNS	N/A	0.0015	N/A	N/A	N/A	N/A
Be (total)	1	38	7.7	0.0042	N/A	0.0042	7.7	0
Cd (diss)	1	0.2	0.039	0.003	N/A	0.003	0.042	0
Cd (total)	1	0.69	0.14	0.0044	N/A	0.0044	0.14	0
Cu (diss)	6	0.086	0.017	15	N/A	15	15	0
Cu (total)	6	6.9	1.4	16	N/A	16	16	0
Zn (diss)	1	4.7	0.94	0.19	N/A	0.19	1.1	0
Zn (total)	1	343	69	0.21	N/A	0.21	69	0
H+ (pH)	6	4.4E-06	9E-07	0.00037	N/A	0.0037	0.00037	0

Table 6B Natural Background (runoff)
Sample point: SCTHC004.50
Bankfull discharge = 4.0 cfs

Parameter	Load Cond (Fig. 5)	Load Capacity (kg/day)	MOS (kg/day)	Nat Back Load (kg/day)	Human-Caused Load (kg/day)	Load Allocation (kg/day)	TMDL (kg/day)	Load Reduction (kg/day)
Be (diss)	N/A	NNS	N/A	0.0011	N/A	N/A	N/A	N/A
Be (total)	1	27	5.5	0.0022	N/A	0.0022	5.5	0
Cd (diss)	1	0.14	0.028	0.0022	N/A	0.0022	0.03	0
Cd (total)	1	0.49	0.098	0.0031	N/A	0.0031	0.1	0
Cu (diss)	6	0.062	0.012	2.9	N/A	2.9	2.9	0
Cu (total)	1	4.9	0.98	3	N/A	3	4	0
Zn (diss)	1	3.4	0.67	0.29	N/A	0.29	0.97	0
Zn (total)	1	245	49	0.15	N/A	0.15	49	0
H+ (pH)	6	3.1E-06	6E-07	0.00034	N/A	0.00034	0.00034	0

Table 6C 3R Mine plus natural background (runoff)
Sample point: SCTHC004.07
Bankfull discharge = 13.7 cfs

Parameter	Load Cond (Fig. 5)	Load Capacity (kg/day)	MOS (kg/day)	Nat Back Load (kg/day)	Human-Caused Load (kg/day)	Load Allocation (kg/day)	TMDL (kg/day)	Load Reduction (kg/day)
Be (diss)	N/A	NNS	N/A	0.0037	N/A	N/A	N/A	N/A
Be (total)	1	94	19	0.0037	0	0	19	0
Cd (diss)	2	0.48	0.096	0.00074	0.016	0.016	0.12	0
Cd (total)	2	1.7	0.34	0.011	0.026	0.026	0.37	0
Cu (diss)	8	0.21	0.042	24	167	0	0.21	167
Cu (total)	8	17	3.4	25	190	0	17	190
Zn (diss)	2	12	2.3	0.74	1.4	1.4	4.4	0
Zn (total)	2	838	168	0.5	1.4	1.4	169	0
H+ (pH)	9	1.1E-05	2.1E-06	0.001	0.0008	0	1.1E-05	0.0008

Table 6D 3R Spring (non-regulateable point source)
Sample point: SCTHC004.01
Baseflow discharge = 0.001 cfs
Note: Existing loads cannot be classified further as natural or human at this discharge.

Parameter	Load Cond (Fig. 5)	Load Capacity (kg/day)	MOS (kg/day)	Existing Load	TMDL (kg/day)
Be (diss)	N/A	1.3E-05	2.6E-06	5.4E-06	8E-06
Be (total)	N/A	0.0028	0.00055	6.6E-06	5.6E-04
Cd (diss)	N/A	3.4E-06	7E-07	1.6E-04	3.4E-06
Cd (total)	N/A	0.00012	2.4E-05	1.4E-04	1.2E-04
Cu (diss)	N/A	1.3E-05	2.5E-06	0.15	1.3E-05
Cu (total)	N/A	0.0012	0.00024	0.14	1.2E-03
Zn (diss)	N/A	0.00017	3.4E-05	3.8E-03	1.7E-04
Zn (total)	N/A	0.061	0.012	3.8E-03	1.6E-02
H+ (pH)	N/A	1E-09	2E-10	2.7E-06	1E-09

Table 6E 3R spring plus upstream sources (runoff)
Sample point: SCTHC004.01
Bankfull discharge = 14.1 cfs

Parameter	Load Cond (Fig. 5)	Load Capacity (kg/day)	MOS (kg/day)	Nat Back Load (kg/day)	Human-Caused Load (kg/day)	Load Allocation (kg/day)	TMDL (kg/day)	Load Reduction (kg/day)
Be (diss)	2	0.18	0.037	0.0038	0.027	0.027	0.067	0
Be (total)	2	39	7.8	0.0091	0.07	0.07	7.9	0
Cd (diss)	7	0.038	0.0075	0.0076	0.92	0	0.038	0.9
Cd (total)	2	1.7	0.34	0.011	1.3	1.3	1.6	0
Cu (diss)	8	0.14	0.027	24	1,620	0	0.14	1,620
Cu (total)	8	17	3.4	25	1,643	0	17	1,643
Zn (diss)	7	1.8	0.36	0.76	30	0	1.8	29
Zn (total)	2	862	172	0.52	32	32	205	0
H+ (pH)	8	1.1E-05	2.2E-06	0.0011	0.0058	0	1.1E-05	0.0058

Table 6F Cox Gulch - Ventura Mine basin (Ventura Mine and other unnamed mines) (nonpoint sources) - Sample point: SCCXG001.04
Bankfull discharge = 6.1 cfs
Note: No H+ measurement taken at this location.

Parameter	Load Cond (Fig. 5)	Load Capacity (kg/day)	MOS (kg/day)	Nat Back Load (kg/day)	Human-Caused Load (kg/day)	Load Allocation (kg/day)	TMDL (kg/day)	Load Reduction (kg/day)
Be (diss)	N/A	NNS	N/A	0.0016	N/A	N/A	N/A	N/A
Be (total)	2	42	8.4	0.004	0.057	0.057	8.4	0
Cd (diss)	2	1.2	0.23	0.0033	0.16	0.16	0.4	0
Cd (total)	2	0.75	0.15	0.005	0.32	0.32	0.48	0
Cu (diss)	8	0.41	0.082	11	17	0	0.41	17
Cu (total)	8	7.5	1.5	11	14	0	7.5	15.5
Zn (diss)	7	19	3.9	0.33	34	0	19	19
Zn (total)	2	373	75	0.22	34	34	109	0
H+ (pH)	1	4.8E-06	1E-06	N/A	N/A	N/A	N/A	N/A

Table 6G Cox Gulch - European Mine basin (European Mine and other unnamed mines) (nonpoint sources)
Sample point: SCCXG000.01
Bankfull discharge = 10.8 cfs
Note: No H+ measurement taken at this location.

Parameter	Load Cond (Fig. 5)	Load Capacity (kg/day)	MOS (kg/day)	Nat Back Load (kg/day)	Human-Caused Load (kg/day)	Load Allocation (kg/day)	TMDL (kg/day)	Load Reduction (kg/day)
Be (diss)	N/A	NNS	N/A	0.0029	N/A	N/A	N/A	N/A
Be (total)	2	74	15	0.007	0.099	0.099	15	0
Cd (diss)	2	1.3	0.26	0.0058	0.15	0.15	0.42	0
Cd (total)	2	1.3	0.26	0.0085	0.19	0.19	0.47	0
Cu (diss)	8	0.49	0.097	19	28	0	0.49	28
Cu (total)	8	13	2.6	20	20	0	13	20
Zn (diss)	7	24	4.8	0.58	30	0	24	12
Zn (total)	2	661	132	0.4	24	24	156	0
H+ (pH)	1	8.5E-06	1.7E-06	N/A	N/A	N/A	N/A	N/A

Table 6H Intermittent reach of Cox Gulch (point source)
Sample point: SCCXG000.85
Baseflow discharge = 0.001 cfs
Note: Existing loads cannot be further classified as natural or human at this discharge.

Parameter	Load Cond (Fig. 5)	Load Capacity (kg/day)	MOS (kg/day)	Existing Load (kg/day)	TMDL (kg/day)
Be (diss)	N/A	1.3E-05	2.6E-06	1.9E-05	1.3E-05
Be (total)	N/A	2.8E-03	5.5E-04	2.4E-05	5.8E-04
Cd (diss)	N/A	1.5E-05	3E-06	9.3E-05	1.5E-05
Cd (total)	N/A	1.2E-04	2.4E-05	1.3E-04	1.2E-04
Cu (diss)	N/A	7.2E-05	1.4E-05	3.2E-02	7.2E-05
Cu (total)	N/A	1.2E-03	2.4E-04	3.3E-02	1.2E-03
Zn (diss)	N/A	9.3E-04	1.9E-04	1.7E-02	9.3E-04
Zn (total)	N/A	6.1E-02	1.2E-02	1.9E-02	3.1E-02
H+ (pH)	N/A	1E-09	2E-10	1.2E-06	0

Table 6I Intermittent reach of Cox Gulch (runoff)
Sample point: SCCXG00.85
Bankfull discharge = 17.1 cfs

Parameter	Load Cond (Fig. 5)	Load Capacity (kg/day)	MOS (kg/day)	Nat Back Load (kg/day)	Human-Caused Load (kg/day)	Load Allocation (kg/day)	TMDL (kg/day)	Load Reduction (kg/day)
Be (diss)	4	0.22	0.044	0.0046	0.17	0.17	0.22	0
Be (total)	2	47	9.5	0.011	0.22	0.22	9.7	0
Cd (diss)	7	0.15	0.029	0.0092	0.66	0	0.15	0.55
Cd (total)	2	2.1	0.42	0.013	1.4	1.4	1.8	0
Cu (diss)	8	0.62	0.12	29	97	0	0.62	97
Cu (total)	8	21	4.2	31	78	0	21	82.2
Zn (diss)	7	8.1	1.6	0.92	116	0	8.1	110
Zn (total)	2	1,046	209	0.63	120	120	330	0
H+ (pH)	8	1.3E-05	2.7E-06	0.0013	0.0023	0	1.3E-05	0.0023

Table 6J 3R Canyon intermittent reach (nonpoint source)
Sample point: SCTHC003.03
Baseflow discharge = 0.11 cfs
Note: No natural background load applicable at this location at this discharge.

Parameter	Load Cond (Fig. 5)	Load Capacity (kg/day)	MOS (kg/day)	Nat Back Load (kg/day)	Human-Caused Load (kg/day)	Load Allocation (kg/day)	TMDL (kg/day)	Load Reduction (kg/day)
Be (diss)	7	1.4E-03	2.9E-04	N/A	2.4E-03	0	1.4E-03	1.3E-03
Be (total)	2	0.3	6.1E-02	N/A	2.2E-03	2.2E-03	6.3E-02	0
Cd (diss)	7	1.3E-03	2.6E-04	N/A	5.1E-03	0	1.3E-03	4E-03
Cd (total)	2	1.3E-02	2.7E-03	N/A	6.5E-03	6.5E-03	9.1E-03	0
Cu (diss)	7	6E-03	1.2E-03	N/A	6.6	0	6E-03	6.6
Cu (total)	7	0.13	2.7E-02	N/A	6.6	0	0.13	6.5
Zn (diss)	7	7.8E-02	1.6E-02	N/A	0.8	0	7.8E-02	0.74
Zn (total)	2	6.7	1.3	N/A	1	1	2.4	0
H+ (pH)	7	8.6E-08	1.7E-08	N/A	1.1E-04	0	8.6E-08	1.1E-04

Table 6K 3R Canyon, Cox Gulch (all upstream sources) (runoff)
Sample point: SCTHC003.03
Bankfull discharge = 42.5 cfs

Parameter	Load Cond (Fig. 5)	Load Capacity (kg/day)	MOS (kg/day)	Nat Back Load (kg/day)	Human-Caused Load (kg/day)	Load Allocation (kg/day)	TMDL (kg/day)	Load Reduction (kg/day)
Be (diss)	2	0.55	0.11	0.011	0.4	0.4	0.53	0
Be (total)	2	117	23	0.028	0.34	0.34	24	0
Cd (diss)	7	0.4	0.079	0.023	0.83	0	0.4	0.54
Cd (total)	2	5.2	1	0.033	1.5	1.5	2.6	0
Cu (diss)	8	1.7	0.35	73	1,929	0	1.7	1,929
Cu (total)	8	52	10	77	2,061	0	52	2,061
Zn (diss)	7	22	4.5	2.3	176	0	22	160
Zn (total)	2	2,599	520	1.6	232	232	753	0
H+ (pH)	8	3.3E-05	6.7E-06	0.0032	0.01	0	3.3E-05	0.01

7.0 IMPLEMENTATION`

This investigation shows that water quality standards will be met when the load reductions are achieved. This first phase investigation has identified the major sources of pollutant loading and quantified contributions so that management decisions can be made.

The target conditions for 3R Canyon are the removal of all mining residue dumps from the streambanks, the removal of all mine-waste originated sediments from the streambed and the isolation and treatment of all mining-impacted groundwater discharges (including springs). While TMDL calculations and values may be different between pollutants, controlling the exposure of the source material to weathering, treating the runoff and removing stream sediments from segments where needed, will reduce all the 303[d]-listed pollutants to within standards or natural background levels.

With the exception of 3R Mine which is privately owned, the pollutant sources in the subject basin are all on Coronado National Forest land. Abandoned mines represent significant technical, legal, and monetary challenges in designing and implementing remedial measures. USFS has a duty to apply for NPDES permits for both active and abandoned mines, on lands under their control, with potential to discharge to surface waters. Such permits would address discharges to surface water from mining haul roads, mine tailing and waste rock piles, and other mining-related facilities. The U.S. Forest Service has a program using CERCLA-driven actions to support remediation of sites causing harm to the ecosystem. This has not been instituted in the subject basin, but is being considered by the Coronado National Forest. If USFS addresses problems at any of these sites through CERCLA, or any other remediation program, specific permits may not be necessary; however, the requirements normally established through a permit are still required to be met.

ADEQ has divided the pollutant sources into categories based upon possible remediation strategies. These suggested strategies are general. Responsible parties must undertake site specific studies before selection, design, and implementation of a remediation method can be accomplished.

1. Mining residue dumps can be remediated by
    a. Removing the material and either hauling to an active mine for processing with ore, or using the material to fill the abandoned mine works.
    b. Leaving the material in place and preventing impacted runoff from reaching the stream. (This has been accomplished fairly successfully by Asarco at Trench Camp Mine.)
2. Combining impacted stream sediments with the mining residue dump material and an acid neutralizing material; e.g., limestone or portland cement, for remediation.

As previously stated, the USGS (personal comm, Floyd Gray, USGS, 05/31/02) has concluded that in addition to mine dump erosion, the accumulation of deposits in the streambed resulting from the evaporation of runoff from abandoned mine sites and discharge from mining-impacted springs is another large contributor to degraded streamflow when re-dissolved during storm events. ADEQ has not made linkages between the spring discharge into the subject stream and a specific mine. Treatment of discharges, for example, through a artificial wetlands has been successfully done elsewhere and would reduce the pollutant loadings.

The second phase investigation will:

- Further develop the characterization of natural background versus human-caused loads;
- Further characterize sources;
- Require NPDES permits for point source discharges;
- Refine load allocations, possibly reclassifying some of the load allocations to wasteload allocations; and,
- Initiate formation of a watershed group focused towards implementation.

ADEQ will pursue collaboration with the USGS to continue its watershed studies in this area, including support for flow and pollutant sampling. ADEQ may conduct additional sampling when climate conditions change from drought to a wetter pattern.

HGC's Model Development Report summary includes several suggestions that should be performed as part of a second phase investigation: "[W]ork that could be undertaken to improve the basis for modeling includes the following:

- *Installation and monitoring of precipitation gauges to determine rainfall intensities and site-specific daily rainfall for comparison with National Weather Service data,*
- *Development and continuous monitoring of stream gauging stations for measuring complete runoff hydrographs, and*
- *Synchronous collection of water quality samples at several locations over the duration of a complete runoff event to determine concentration as a function of location and discharge.*"

In sum, achieving the target conditions will reduce the human-caused loads to within standards. Additional monitoring and investigation will further develop ADEQ's understanding of loading due to natural background causing exceedences and where and when this might happen.

8.0 PUBLIC PARTICIPATION AND RESPONSIVENESS SUMMARY

Development of the 3R Canyon TMDL included public participation in accordance with 40 CFR Parts 25 & 130.7. Public participation included review and input from stakeholder groups. Multiple presentations and meetings were held by the ADEQ in 1997 and 2001. These meetings were attended by owners/operators of mining sites, property owners; environmental groups; representatives of local, state, and federal agencies; and other interested members of the public. Written documentation of public participation is on file with ADEQ's Hydrologic Support and Assessment Section, located at 1110 W. Washington Street, 5th Floor, Phoenix, Arizona 85007.

Additionally, ADEQ released a draft of this report in December, 2001. Response to this document revealed ADEQ should:

- More clearly explain the concentration extrapolation methodology.
- Clarify its understanding of natural background conditions.
- Clearly show the linkages between sample sites and sources.

Considering this concerns and the fact that recently approved changes in Arizona surface water quality standards would affect the study, ADEQ rewrote this TMDL report and is releasing this second draft for comments.

9.0 BIBLIOGRAPHY AND REFERENCES

For availability and price information of ADEQ documents, call (602) 207-2202.

ADEQ, “Analysis of Water Quality Limited Waters in the Sonoita Creek Watershed near Patagonia, Santa Cruz County, Arizona Phase I - Confirmatory Sampling of 303[d]-Listed Parameters,” October, 1998, Phoenix, Arizona.

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U.S. Geological Survey Administrative Report “Preliminary Assessment/Site Inspection of the Alum Gulch - Flux Canyon Watershed, Northern Patagonia Mountains", Floyd Gray, Laura Norman, Oscar Duarte, Ailiang Goo, and Maurice Chafee, July 2002 (in press).

U.S. Geological Survey “Study and Interpretation of the Chemical Characteristics of Natural Water,” Water-Supply Paper 2254, John D. Hem,1989.

Personal communications with personnel of the Arizona Department of Mines and Minerals, Phoenix, Arizona. Various dates over the course of the project.

Contractor-prepared reports are available for viewing in their entirety at the Hydrologic Support and Assessment Section, 3rd floor, ADEQ, 3033 N. Central, Phoenix, Arizona. Copies can be made available on request and are subject to a State-required copying fee.

APPENDIX A - Data Collection

Sample Sites

Figure 3 is a map of the subject basin with sample site locations. Sample sites were selected to permit meeting of project goals. ADEQ has developed a system of surface water sample point I.D.s:

Site ID: bbsssddd.d *bb* = basin ("SC" is the Santa Cruz River); *sss* = stream code (e.g.: "SCTHC" for Three R Canyon); *ddd.dd* = distance from stream mouth in stream miles along the stream channel as measured on U. S. Geological Survey maps in a scale of 1:24,000.

Sample points are listed in order from most upstream to most downstream. Where appropriate, tributary sample points are inserted between the sample points bracketing the mouth of the tributary. Complete locational data including latitude, longitude, UTM, or HUC, is stored in the project files in tabular format and available for the cost of copying from ADEQ.

SCUTH000.30	Upstream from 3R Mine (north tributary): natural background sample as area appears geologically similar to the rest of the basin and undisturbed by mining
SCTHC004.50	Upstream from 3R Mine (south canyon): natural background sample as area appears geologically similar to the rest of the basin and undisturbed by mining
SCTHC004.07	Upstream from intermittent reach; downstream of 3R Mine: natural background plus 3R Mine
SCTHC004.01	Upstream end of intermittent reach: groundwater (spring) + natural background + 3R Mine
SCCXG001.04	Cox Gulch, upstream from mouth of European Mine tributary (unnamed): natural background + Ventura Mine
SCUCX000.01	European Mine tributary (unnamed): natural background + European Mine
SCCXG000.85	Cox Gulch, downstream from mouth of European Mine tributary (unnamed): groundwater (spring) + natural background + European and Ventura Mines
SCTHC003.03	Downstream from Cox Gulch mouth: subject basin

Sample Collection Procedures and Equipment

The targeted parameters are those for which each stream is considered impaired as reported on the 303[d] List. Tributaries were monitored for the listed parameters of the downstream waters.

ADEQ followed the current USEPA-approved Quality Assurance Project Plan (QAPP) (May, 1991) and the ADEQ Fixed Station Network Procedures Manual derived from the QAPP. These contain the sampling techniques ADEQ is required to follow and which were followed as part of this project.

Commentors have suggested that ADEQ should follow EPA Method 1669, “Sampling Ambient Water for Determination of Trace Metals at EPA Water Quality Criteria Levels”, EPA 821-R-95034 (1995) when collecting metals data. Method 1669 states: "*This method is not intended for determination of metals at concentrations normally found in treated and untreated discharges from industrial facilities. Existing regulations (40 CFR parts 400-500)* *typically limit concentrations to the mid to high part-per-billion (ppb) range, whereas ambient metals concentrations are normally in the low part-per-trillion (ppt) to low ppb range.*"

Due to the heavy mining and ore processing activity in the subject basins, the concentrations of the listed metals are in the high part-per-billion range. The relevant standards for the subject streams are within the detections limits for standard EPA methods as opposed to the specialized 1600-series methods.

There were instances where results for dissolved metals are greater than those for total metals which raised questions about the validity of the reported data. The dissolved concentrations are larger than the total concentrations due to rounding in reporting and because some samples were diluted due to matrix interference (personal comm, Carie Wilson, Bolin Laboratories, 01/23/98). Conversations with ADEQ's QA/QC Unit and the laboratory staff determined that the data is still valid.

Field Measurements and Equipment

Field water quality data was obtained with a Hydrolab Surveyor. These measurements are:

- water temperature (C)
- dissolved oxygen (mg/L & % saturation)
- specific conductance (µmhos)
- pH (a field measurement due to holding time of 15 minutes)

Other field measurements:

- Air temperature (C)
- Flow with either a Marsh-McBirney current velocity meter or, in cases of very low or very high discharge, a flow measurement was not possible and an estimate was made by field personnel.
- A hand-held Global Positioning System (GPS) receiver was used to locate sample sites.

All field measurements and observations were recorded on field sheets. All sites were photographed during each visit.

Laboratories and Analytical Methods

ADEQ is required (A.A.C. R18-11-111) to use an approved analytical method and a laboratory that is licensed by the Arizona Department of Health Services (DHS). For the subject waterbodies, ADEQ used the DHS laboratory and Bolin, a DHS-licensed laboratory.

Bolin Laboratories, Inc.	Arizona State Health Laboratory
1763 N. 25th Avenue	1520 W. Adams
Phoenix, Arizona 85023	Phoenix, Arizona 85007

Hardness data is necessary to evaluate the metals data because surface water quality standards for certain parameters change because toxicity varies with hardness. The higher the hardness, the lower the toxicity . EPA guidance and Arizona's surface water quality standards bracket the hardness values from 25 mg/L to 400 mg/L as $CaCO_3$. Further study is needed to determine whether the hardness equations for these metals hold for a hardness values exceeding 400 mg/L as $CaCO_3$. Hardness was calculated from the calcium and magnesium concentrations in accordance with the "Standard Methods for the Examination of Water and Wastewater", 19th Edition, 1995.

The laboratory analytical methods were used in this project were:

Metals (Totals): Ca, Fe, Mg, Zn (USEPA method 200.7)
Metals (Totals): Be, Cd, Cu (USEPA method 200.9)
Metals (Dissolved): Zn (USEPA method 200.7)
Metals (Dissolved): Be, Cd, Cu (USEPA method 200.9)

Quality Control

At least one set of quality control blanks and split samples were collected during each sample event. Split samples were collected (using an USGS-designed churn splitter) as a check on laboratory accuracy. This is a sample split between two bottle sets which can reasonably be assumed to be identical (within 10%) of each other. All splits were within acceptable tolerances. "Blanks" were collected to verify the efficacy of field decontamination and equipment cleanliness.

ADEQ also split some samples with Asarco as a courtesy to Asarco. These were not part of the project quality assurance splits and blanks which were collected at other sample points. In one instance, zinc was detected in a blank collected at Asarco’s request, and was determined to be a result of contamination of the rinse water supplied by ADHS. The detected concentrations (in the rinse water) were 20 to 40 Fg/L while the stream concentration was over an order of magnitude higher at 470 Fg/L.

Checking all calculations and data entry was done by staff. All field equipment is maintained and calibrated on a regular basis to ensure valid field measurements. Calibration information is logged in the record book for each individual instrument.

APPENDIX B - Calculation of Concentration Extrapolation Factors

Due to the lack of precipitation and the ephemeral nature of the subject streams, very few sample points were sampled more than once and most measurements were made under baseflow conditions in the intermittent (groundwater-fed) reaches of these streams. These limited measurements were used as the basis for calculating (extrapolating) concentrations at higher (bankfull) flows. In order to model loads under the identified critical flows of baseflow and bankfull (high) flow, a means other than a direct linear relationship was established to calculate an estimated bankfull flow concentration from the measured low flow concentration at each sample point.

The sample point in the subject stream with measurements under both high and low flow conditions (SCTHC004.01) was identified and those measurements used to calculate a bankfull concentration extrapolation factor. Two methods of deriving this factor were tested: a flow-weighted factor and an average ratio factor. The bankfull concentration calculated was tested against the measured bankfull concentrations at that sample point. The factor which yielded the greatest overall accuracy for each stream is used to calculate the bankfull concentration estimates. The accompanying tables, formulae, examples and the logic behind the selection of each factor are explained by stream.

The bankfull concentration for each sample point was calculated by multiplying the selected factor by the measured baseflow concentration. This extrapolated bankfull concentration is then inserted into the loading model. The value 0.0024465 is a units adjustment factor to get from g/L and cubic feet per second (cfs) to kg/day:

(conc) F*g/L* ◊ *1.0 x 10*$^{-9}$ *kg/*F*g* ◊ *28.316 L/ft*^{3} ◊ *(flow) ft*^{3}*/sec* ◊ *86400 sec/day x concentration extrapolation factor*

which works out as:

[0.0024465] x conc(mg/L) x flow(ft^3*/sec) x concentration extrapolation factor = load in kg/day*

The general relationship, or trend, of the concentrations of each parameter with changes in flow was determined using linear regression. Due to insufficient data, the resulting "best-fit" line was used solely as an indicator of general direction of change; i.e., increasing or decreasing, with increasing discharge. ADEQ intends to conduct additional monitoring in the subject basins and will adjust the TMDL as needed when the additional data is considered.

The following extrapolation factors were calculated for 3R Canyon; an explanation and example of the methodology follows.

Flow Extrapolation Factors for 3R Canyon Investigation

Parameter	3R Canyon (Factors)	Cox Gulch (Factors)
Hardness	0.706	0.298
H+	0.173	0.173
Beryllium (diss)	0.446	0.554
Beryllium (total)	0.443	0.557
Copper (diss)	0.791	0.231
Copper (total)	0.834	0.195
Cadmium (diss)	0.431	0.431
Cadmium (total)	0.638	0.638
Zinc (diss)	0.579	0.395
Zinc (total)	0.597	0.379

The following formulae were used to calculate flow extrapolation factors. The absolute value of the calculated extrapolation factor is used:

parameter(weightedfactor) =

$$\frac{\dfrac{3\text{(High Flow Concentration x High Flow Discharge)}}{3\text{High Flow Discharge}} - \dfrac{3\text{(Low Flow Concentration x Low Flow Discharge)}}{3\text{Low Flow Discharge}}}{\dfrac{3\text{(Low Flow Concentration x Low Flow Discharge)}}{3\text{Low Flow Discharge}}}$$

Parameter(weightedcalc) = Parameter(weightedfactor) x Parameter(baseflow average)
Parameter(weightederror) = (Parameter(meas) - Parameter(weightedcalc)) ÷ Parameter(meas)
Weighted Error of each stream is calculated using the absolute value of each individual error.

Parameter(avgfactor) = average of Parameter(higher flow) ÷ average of Parameter(baseflow)
Parameter(avgcalc) = Parameter(avgfactor) x Parameter(baseflow average)
Parameter(avgerror) = (Parameter(meas) - Parameter(weightedcalc)) ÷ Parameter(meas)
Average Error of each stream is calculated using the absolute value of each individual error.

Hardness

Hardness is calculated from calcium and magnesium in units of mg/L $CaCO_3$ equivalent. When hardness is used to calculate standards for certain metals, the hardness is always the calculated value or 400 mg/L, whichever is lesser. For example, a calculated hardness of 2666 is **not** used to calculate a standard, instead 400 is used to calculate the standard, but a calculated hardness of 208 **is** used to calculate the standard. (Arizona Surface Water Quality Standards: title 18, chapter 11, A.A.C.).

In 3R Canyon, measured concentrations exhibit a numerically significant difference (roughly one order of magnitude) between base flow and high flow. 3R Canyon basin has a minimal relationship between hardness and flow; however, when separated into 3R Canyon and Cox Gulch sub-basins, a clearer relationship can be observed. The 3R Canyon data would be best extrapolated using the average ratio and the Cox Gulch data using the flow weighted method. When all the data is plotted against flow, the general data trend is maintained by the extrapolated data.

Flow Weighting

Site ID	**Date**	**Discharge (cfs)**	**Flow**	**Hard (meas)**	**Hard (weighted factor)**	**Hard (weighted calc)**	**Hard (weighted error)**
SCCXG000.85	1/10/00	0.001	base	927			
SCCXG000.85	7/21/99	0.06	higher	292		276	5%
SCTHC004.01	12/5/97	0.001	base	72	0.298	19	
SCTHC004.01	6/1/98	0.001	base	52			
SCTHC004.01	1/11/00	0.001	base	63			
SCTHC004.01	4/1/98	0.02	higher	46			59%
SCTHC004.01	7/21/99	0.02	higher	43			56%
SCTHC004.01	2/4/98	0.04	higher	43			56%
SCTGC003.03	4/1/98	0.11	base	412			
SCTGC003.03	2/4/98	0.93	higher	206		123	40%
					weighted error		43%

Example: Hard(weighted factor) =

$$\frac{\dfrac{\{(46 \times 0.02) + (43 \times 0.02) + (43 \times 0.04)\}}{(0.02 + 0.02 + 0.04)} - \dfrac{\{(72 \times 0.001) + (52 \times 0.001) + (63 \times 0.001)\}}{(0.001 + 0.001 + 0.001)}}{\dfrac{\{(72 \times 0.001) + (52 \times 0.001) + (63 \times 0.001)\}}{(0.001 + 0.001 + 0.001)}} = \mathbf{0.298} \text{ conc extrap factor}$$

Hard(weightedcalc) = Hard(weighted factor) x Hard(baseflow avg) = 0.298 x {(72+52+63) / 3} = **18.6** => **19** mg/L
Hard(weightederror) = (Hard(meas) **-** Hard(weighted calc)) ÷ Hard(meas) = (46 **-** 19) / 46 = **59%** error
Weighted Error of each stream is calculated using the absolute value of each individual error.

Average Ratio

Site ID	Date	Discharge (cfs)	Flow	Hard (meas)	Hard (weighted factor)	Hard (weighted calc)	Hard (weighted error)
SCCXG000.85	1/10/00	0.001	base	927			
SCCXG000.85	7/21/99	0.06	higher	292		654	124%
SCTHC004.01	12/5/97	0.001	base	72	0.710	44	
SCTHC004.01	6/1/98	0.001	base	52			
SCTHC004.01	1/11/00	0.001	base	63			
SCTHC004.01	4/1/98	0.02	higher	46			4%
SCTHC004.01	7/21/99	0.02	higher	43			2%
SCTHC004.01	2/4/98	0.04	higher	43			2%
SCTGC003.03	4/1/98	0.11	base	412			
SCTGC003.03	2/4/98	0.93	higher	206		291	41%
						Avg error	35%

Hard(avgfactor) = average of Hard(high flow) ÷ average of Hard(low flow)
Example: Hard (avgfactor) = ((46 + 43 + 43) / 3) / ((72 + 52 + 63) / 3) = **0.71** concentration extrapolation factor
Hard(avgcalc) = Hard(avgfactor) x Hard(baseflow average) = 0.71 x {(72+52+63) / 3} = **44.3** => 44 mg/L
Hard(avgerror) = (Hard(meas) **-** Hard(weightedcalc)) ÷ Hard(meas) = (46 **-** 44) / 46 = **4%** error
Average Error of each stream is calculated using the absolute value of each individual error.

pH (as H^+)
$10^{(-pH)} \times 1000 = H^+$ concentration in mg/L
3R Canyon measured pH exhibits a slight increase with an increase in flow. The flow-weighted extrapolation factor better represents this increase; the average ratio extrapolation factor causes a slight decrease in pH with increased flow. When all, including extrapolated, data is plotted against flow, the general data trend is maintained by the extrapolated data.

Beryllium
3R Canyon (including Cox Gulch) measured concentrations exhibit a slight increase in with an increase in flow. When separated into 3R Canyon and Cox Gulch sub-basins, a clearer relationship can be observed in Cox Gulch, but 3R Canyon has no apparent relationship between beryllium concentration and flow. In the Cox Gulch basin, beryllium concentration tends to decrease as discharge increases. The 3R Canyon data would be best extrapolated by using the flow-weighted extrapolation factor and the Cox Gulch data would be best extrapolated by using the average ratio extrapolation factor.

Cadmium
Based upon the available data, measured concentration generally tends to decrease as discharge increases in the subject basin. In both 3R Canyon and Cox Gulch, the dissolved data would be best extrapolated by using the flow-weighted extrapolation factor and the total data using the average ratio extrapolation factor. When all, including extrapolated, data is plotted against flow, the general data trend is maintained by the extrapolated data.

Copper
Based upon the available data, measured concentration generally tends to decrease as discharge increases in the subject basin. The 3R Canyon data would be best extrapolated by using the average ratio extrapolation factor and the Cox Gulch data would be best extrapolated by using the flow-weighted extrapolation factor. When all, including extrapolated, data is plotted against flow, the general data trend is maintained by the extrapolated data.

Zinc
Based upon the available data, measured concentration generally tends to decrease as discharge increases in the subject basin. The 3R Canyon data would be best extrapolated by using the average ratio extrapolation factor and the Cox Gulch data would be best extrapolated by using the flow-weighted extrapolation factor. When all, including extrapolated, data is plotted against flow, the general data trend is maintained by the extrapolated data.